On the coupling of rotovibrational motions in He–Li₂ inelastic collisions

F. A. Gianturco, S. Serna, G. Delgado-Barrio, and P. Villarreal

Citation: *The Journal of Chemical Physics* **95**, 5024 (1991); doi: 10.1063/1.461690

View online: <https://doi.org/10.1063/1.461690>

View Table of Contents: <http://aip.scitation.org/toc/jcp/95/7>

Published by the *American Institute of Physics*

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these
environmentally friendly adhesive
systems can do

READ NOW

PRESENTED BY
MASTERBOND
ADHESIVES | SEALANTS | COATINGS

On the coupling of rotovibrational motions in He-Li₂ inelastic collisions

F. A. Gianturco and S. Serna^{a)}

Department of Chemistry, The University of Rome, 00185 Città Universitaria, Rome, Italy

G. Delgado-Barrio and P. Villarreal

Instituto de Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain

(Received 8 May 1991; accepted 12 June 1991)

He-Li₂ interaction potentials, which explicitly include both angular anisotropy and internal vibrational coordinates, have been proposed recently in the literature by extracting them from laser-selected, crossed beam experiments and from the use of various perturbation expansions. In view of the importance of assessing as accurately as possible the dynamical coupling of such internal degrees of freedom during inelastic, low-energy collisions, the present study undertakes a detailed computational comparison of the various possible decoupling schemes which can be employed to treat the above processes. It is found that because of the rather weak nature of the interaction in the title system, nearly all schemes work reasonably well and can be used in scattering calculations. It is, however, shown that the previously suggested potentials need to be modified extensively in order to yield cross sections which agree with the experimental findings.

I. INTRODUCTION

The existence and the refinements of crossed molecular beam experiments over the last 30 years have provided us with a rather sophisticated understanding of the detailed, microscopic mechanisms which preside over molecular elastic collisions and rotationally inelastic collisions, as well as reactive molecular encounters. Such experiments, in fact, have been capable of relating specific features of the interaction forces between molecular partners to selected outcomes of the scattering process.^{1,2} Because of the necessary, and significant, cooling of the internal degrees of freedom which occurs during the supersonic expansion, both experiments and theory, however, have treated the molecular targets as being mostly in their ground vibrational levels and therefore the majority of the available data and of the reliable calculations have considered the ensuing dynamics as that of vibrationally "cold" molecules.

In the last ten years or so, however, the use of chemical lasers and of infrared laser excitation techniques have allowed experimentalists to begin a more systematic investigation on the scattering processes which involve "hot" molecules in vibrationally excited states during the collisions³⁻⁶ and therefore one is beginning to gather new and valuable information on the energy transfer pathways for highly vibrationally excited species in the electronic ground states. A recent review on experimental methods⁷ summarizes very effectively the present body of knowledge on the relaxations during collisions of internal energy accumulated in the vibrational degrees of freedom.

From the theoretical point of view, on the other hand, the situation is still rather complicated and far from being fully understood. One knows that, in principle, the "super-molecule" made by the colliding partners during encounters contains all the required information on the coupling

between relative motion and the vibrational coordinates, as well as the information on the rotational torque applied to either partner by the approaching projectile. In practical terms, however, only in very few cases one has been able to construct the actual dependence of the coupling on the collisional variables. A more detailed interpretation of the effect of vibrational excitation on the collision dynamics, in fact, depends both on a reliable potential energy surface (PES) for a broad range of values of the specific internal coordinate involved Q_i and accurate scattering calculations. The overwhelming majority of the available potentials, on the other hand, have been determined for a target molecule (usually a diatomic molecule) in its ground vibrational state. For the case of neutral interactions, in fact, *ab initio* calculations of the PES for a large range of the intramolecular distance r do not seem to exist and must therefore be evaluated semiempirically. The existing examples even for the latter approach, however, are still rather few and only for fairly simple systems, e.g., H₂-He and Ne,⁸ Na₂-He, and Ne and Ar.⁹

It therefore becomes of interest to try to work out a detailed study on the role that such empirical choices of the dynamical coupling have during actual scattering processes and how the various possible approximations which can be used to simplify the collision calculations are affected by the above choices. In order to carry out such a study, however, it is necessary to be able to rely on good quality experimental information that could provide us with explicit evidence of the dependence of scattering observables on the molecular vibrational coordinates.

Recently, in fact, such studies have been performed in a systematic way by examining the influence of vibrational excitation of electronic ground-state molecules on the inelastic cross sections produced in their collisions with rare gases.¹⁰⁻¹² The authors expanded an intense beam of Li₂ molecules into a vacuum apparatus for molecular beam experiments and generated highly vibrationally excited molecules via Franck-Condon pumping (FCP) by the use of a continuous wave (CW) single-mode dye laser.

^{a)} IBM-ECSEC Visiting Fellow. Permanent address: Instituto de Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain.

Following the pump process, the primary beam was attenuated in a collision cell by the rare gases He and Kr. Behind a small aperture, the change in intensity of the laser-induced fluorescence (LIF) for the different vibrational states was measured by using a second CW single-mode dye laser. By simply applying Beer's law, the percentage change of the integral cross section for each vibrational state was thus derived.

What was found for the rare gas partners was that the total cross sections (i.e., those summed over all rotational and vibrational processes at the given collision energy) first decreased with increasing vibrational excitation then reached a minimum and subsequently increased towards the largest values of vibrational states of the target. It is interesting to note that such behavior was observed in measurements of both differential and integral cross sections.^{10,11}

The above experimental data were interpreted in terms of specific features of the PES involved and of the relative changes of the attractive and repulsive parts of the surfaces as the vibrational states of the target molecule were changed.¹³ It was, however, rather difficult to disentangle the separate effects of PES feature changes and of the dynamical approximations employed to compute inelastic cross sections via those potential functions. In the present work, therefore, we have decided to undertake such a study on the He-Li₂ system, for which various forms of PES have been suggested by interpreting the above experiments and to examine the consequences of different dynamical approximations on the general behavior or the computed cross sections. An interesting result of the present study is the discovery of the essentially impulsive nature of the dynamical coupling which acts at the energies of the experiments for the title system. Thus, we will be able to show that different degrees of freedom can be effectively decoupled and that the more simple types of scattering calculations are already sufficient to qualitatively describe the processes at hand. On the other hand, we will also show that currently used anisotropic potentials are not yet accurate enough to uniquely reproduce experimental findings at a quantitative level.

This work is organized as follows: the next section describes the potential functions suggested by previous studies for He-Li₂ and the qualitative interpretation of their dependence on the vibrational coordinate. Section III reports our scattering models and the various forms of alternative coupling schemes, while Sec. IV shows the present results and their comparison with experiments. The general conclusions of our work are summarized in Sec. V.

II. THE POTENTIAL ENERGY FUNCTIONS

As discussed before, full *ab initio* hypersurfaces showing the dependence on all three Jacobian coordinates, i.e., the mean internuclear distance r , the atom-molecule distance R , and their relative orientation $\gamma = \arccos(\hat{R} \cdot \hat{r})$ are not available for the Li₂-Rg systems in general, while for Li₂-He, some accurate calculations have been carried out at the rigid-rotor (RR) level, i.e., by freezing the r values at the molecular equilibrium value r_{eq} .¹⁴ By using the above points as a reference set for estimating potential anisotropy, Fuchs and Toennies¹⁰ have in fact reported a simple extension for a

vibrational-dependent form of PES that separates the potential into its long-range (LR) attractive V_{att} and short-range (SR) repulsive V_{rep} parts. In the LR part, the vibrational motion was included by using v -dependent van der Waals coefficients $C_6(v)$, with v being the vibrational quantum number of the chosen target state. The latter dependence was in turn calculated, together with its anisotropy, from the known v dependence of the static Li₂-dipole polarizabilities.¹⁵ The inclusion of orientational dependence, and of v -dependence, in the SR part of the interaction was performed by accounting for the shift of the repulsive wall to larger R values in the collinear geometry as a consequence of bond-stretching in the vibrationally excited target molecules. In the C_{2v} , perpendicular orientation, they found that the position of the repulsive wall shifted inwards with increasing v values and they associated a shift parameter f to this particular effect. In conclusion, they produced the following form of model potential:

$$V_i(R, r) = E_i [3\rho_i(R, r)^{-8} - 4C_i(r)g_i(R) \times \rho_i(R + Z_r(\Delta r/2), r)^{-6}] \quad (1)$$

The index i labels the $C_{\infty v}(\parallel)$ and $C_{2v}(\perp)$ geometries of the atom-diatomics system and the corresponding parameters. Thus, one has that

$$\rho_{\parallel}(R, r) = \frac{[R - (\Delta r/2)]/Rm_{\parallel} - \beta_{\parallel}}{1 - \beta_{\parallel}} \quad (2a)$$

$$\rho_{\perp}(R, r) = \frac{[R + f(\Delta r/2)]/Rm_{\perp} - \beta_{\perp}}{1 - \beta_{\perp}} \quad (2b)$$

where Rm_i are the positions of the potential minima, ϵ_i the values of the corresponding well depths, and β_i are parameters which take into account the finite extension of the hard-wall repulsion between atomic cores.¹⁰ The Δr values are given by $(r - r_{eq})$ for each vibrational state of the target. Also note that a cut-off function is present via the g_i terms which are given by

$$g_i(R) = \frac{1}{1 + (3.5 \text{ \AA}/R)^{12}}, \quad i = \perp, \quad (3a)$$

$$= 1, \quad i = \parallel. \quad (3b)$$

Finally, the z_i parameters are given by $z_{\parallel} = 1$ and $z_{\perp} = -f$. Thus, the only disposable parameter present in the above potential, which from now on will be called the Fuchs and Toennies (FT) potential energy surface, is given by the value of f that essentially controls the behavior of the repulsive wall in the perpendicular geometry.

The FT potential therefore considers the effect of the target vibrational state on interaction as giving rise to a shift of the repulsive wall to greater R values in the collinear geometry due to the stretching of the vibrationally excited molecule. In the perpendicular orientation, on the other hand, the position of the repulsive wall was found by the authors to shift inwards by increasing the index v of the vibrational state. This further shift was then parametrized by the arbitrary quantity f shown in Eq. (2b).

It is interesting to note at this point that the time-honored way of treating vibrationally inelastic scattering without coupling the collision to rotations describes the interac-

tion via simple spherical atom-atom potentials.¹⁶⁻¹⁸ In the case of collinear geometry, then one defines the distance R_0 between the projectile and the nearest atom of a homonuclear target and the distance $R' = R_0 + r_{eq}/2$, with r_{eq} being the bond equilibrium value at $v = 0$. The corresponding Born-Mayer potential¹⁸ is then given by

$$\begin{aligned} V_{eq}(R') &= A_{||} \exp(-\alpha_{||} R') \\ &= A_{||} \exp[-\alpha_{||} (R_0 + r_{eq}/2)] \\ &= A_{||} \exp(-\alpha_{||} r_{eq}/2) \exp(-\alpha_{||} R_0) \\ &= A_{eq,||} \exp(-\alpha_{||} R_0). \end{aligned} \quad (4)$$

When the target is vibrationally excited, then $r \neq r_{eq}$ and $r = r_{eq} + \Delta r$. The corresponding atom-atom distance R_0 then becomes

$$R_v = R_0 - \Delta r_v/2; \quad (5a)$$

thus

$$\begin{aligned} V_v(R') &= A_{||} \exp(-\alpha_{||} R') \\ &= A_{||} \exp[-\alpha_{||} (R_0 - \Delta r_v/2 + r_{eq}/2)] \\ &= A_{eq,||} \exp[-\alpha_{||} (R_0 - \Delta r_v/2)], \end{aligned} \quad (5b)$$

where $\Delta r_v = r_v - r_{eq}$, with r_v being the average bond distance for the v th vibrational state $\langle r \rangle_v$. One therefore sees from the above result that the collinear potential becomes more repulsive as v increases, since at each collision energy the corresponding turning point moves in to smaller R' values. This is often called the dumbbell model (DM) for the vibrational excitation of diatomic targets in collision with structureless atomic projectiles.

When one now considers the C_{2v} geometry for a homonuclear target, then the corresponding atom distance from the bond midpoint R' is simply given by

$$R' = (R_0^2 - r_{eq}^2/4)^{1/2}, \quad (6)$$

with the usual meaning of R_0 as the atom-atom distance. The corresponding potential is then given by

$$V_{eq}(R') = A_{\perp} \exp[-\alpha_{\perp} (R_0^2 - r_{eq}^2/4)^{1/2}]. \quad (7)$$

When the target molecule is vibrationally excited, then one can write a new expression for the R' distance of Eq. (6), i.e.,

$$\begin{aligned} R' &= [R_v^2 - (r_{eq}/2 + \Delta r_v/2)^2]^{1/2} \\ &\simeq [R_v^2 - r_{eq}^2/4 - r_{eq}\Delta r_v/2]^{1/2}. \end{aligned} \quad (8)$$

Comparing the latter equation with Eq. (6), one then obtains that

$$R_v^2 = R_0^2 + (r_{eq}\Delta r_v/2), \quad (9)$$

where R_v is now the distance between the projectile and either molecular atom for the particular vibrational state v .

Qualitatively, one could therefore say that the overall potential of Eq. (7) becomes less repulsive as v increases, a feature that gives the DM behavior for the C_{2v} geometry. The above discussion therefore shows that the FT potential introduced from the experimental parametrization¹⁰ essentially follows the DM description of the vibrational coupling and tries to further introduce orientational anisotropy from

available HF calculations and from the behavior of the dispersion coefficients.

A pictorial representation of the shape of this PES is given in Fig. 1, where the FT potential is shown in the regions around the well for the two orientations C_{2v} (dashed lines) and $C_{\infty v}$ (solid lines). Two different vibrational states of the target are considered, $v = 0$ and $v = 20$, and two different values for the f parameter of Eqs. (1) and (2) are represented.

One sees clearly the following features:

(i) As the vibrational energy "content" of the target increases, the collinear geometry shows a marked increase in its repulsive part and a corresponding outward shift of the well minima;

(ii) the C_{2v} geometries, on the other hand, exhibit the opposite effect, as their well minima become deeper and move to smaller distances;

(iii) larger values of the arbitrary f parameter in the model potential appear to damp the effects of the increasing v values, since they produce stronger repulsive forces for the $v = 0$ states in both orientations. Thus, they are also markedly affecting the overall anisotropy of the full PES.

We will see below that the choice of the latter free parameter is really modifying the efficiency of the potential in coupling vibrational and angular variables during the collision process.

FIG. 1. Behavior of the well region of the FT potential defined in the text as a function of the vibrational state v of Li_2 and of the relative orientations (C_{2v} and $C_{\infty v}$) of the He-Li_2 system. The top diagrams refer to the $f = +1$ case in Eq. (2), while the bottom diagrams are for the $f = +3$ case.

A partial modification of the FT potential of above was introduced later on by Rubhan and Toennies¹³ in an attempt to generalize the above behavior to the whole series of rare gases colliding with Li_2 . The authors had observed that in the earlier model, the experimental total integral cross section was represented adequately when f was set equal to $+2$. However, it was not able to describe well, as mentioned before, the angular dependence of the cross sections for the vibrationally excited molecules.¹¹ They therefore decided to introduce a further parameter in the repulsive part of the potential function in the collinear orientation and performed with this new choice a further fit of the experimental data. The improvement was not very marked and therefore we decided to limit the present analysis to the earlier FT potential, as too many parameters in the potential would make more confusing the present study of the physical coupling.

A more drastic modification of the FT interaction was also carried out very recently¹⁹ by directly expanding the repulsive and attractive parts of the potential in a two-term Legendre expansion and connecting them via the generalized damping function proposed by Tang and Toennies.²⁰ The final potential function turned out to be less attractive than the FT potential and exhibited an antidumbbell (ADM) behavior, i.e., the collinear orientation becomes more attractive as v increases and the C_{2v} orientation shows a more repulsive character as the v values increase. This is shown in the top part of Fig. 2, where the f parameter has the same meaning as in the FT potential and this alternative potential is labeled the Rubhan (RBN) potential. The $f = +2$ value is the one recommended in Ref. 19 as being the most reliable choice to describe the potential anisotropy.

Just to see how different the ADM behavior is from the more familiar, qualitative dumbbell model, the bottom part of the figure shows the same RBN potential with the f parameter sign changed. Both well depth and position are now shifted to deeper and shorter values, respectively, and their dependence on the vibrational energy content of the target follows the same behavior of the potential of Fig. 1. We believe that there is no physical reason for choosing an ADM behavior in the present model potentials and therefore selected to employ the RBN surface with negative f values. It appears that the calculations of cross sections reported in Refs. 19 and 21 were also carried out with negative values of the f parameter in the repulsive potentials.²²

$$V_{\parallel}(R_{\parallel}, v) = A_{\parallel} \exp[-\alpha_{\parallel}(R_{\parallel} + \Delta r_v)], \quad (10a)$$

$$V_{\perp}(R_{\perp}, v) = A_{\perp} \exp[-\alpha_{\perp}(R_{\perp} - f\Delta r_v)], \quad (10b)$$

where the various symbols have the same meaning as in Eq. (2). Their specific values have been given and discussed in a previous paper¹⁹ and will not be repeated here.

In conclusion, the experiments that were recently carried out to study the dependence of collision cross sections on the internal energy content of the target molecule¹⁰ have proposed a model for the underlying full potential function and such a function has been later generalized by incorporating different criteria for connecting the repulsive and attractive parts of the PES.¹⁹ Both surfaces, however, provide a rather unsatisfactory interpretation of experimental findings

FIG. 2. The same general diagrams as in Fig. 1, but for the RBN potential of Ref. 19 discussed in the main text. The meaning of all the symbols is also the same as in Fig. 1.

once used within a rather simple treatment of the dynamics¹¹ and their overall validity or reliability still remains to be tested.

In the following section, we summarize briefly possible schemes which can be used to treat the quantum dynamics relevant to the present system and to test various features of the PES.

Since we wanted to start from the results of the previous work on this system, we have chosen to vary the parameter f around the optimal values suggested in Refs. 10 and 21. The shapes of the potential functions for such values of f are shown in Fig. 3 for both the FT and the RBN surfaces.

One sees clearly there that the FT potential becomes more anisotropic as v increases and exhibits rather weak anisotropy for $v = 0$. The RBN function, on the other hand, is markedly more anisotropic for the lower vibrational levels, but changes rather little as v increases. Both surfaces show, however, a very clear DM behavior in the sense discussed previously.

III. THE DYNAMICAL MODELS

If one considers the general problem of rotationally and vibrationally inelastic collisions in the case of an atom-diatomics system,²³ the standard space-fixed (SF) formulation of the coupled-channel (CC) expansion leads to the following set of coupled differential equations:

FIG. 3. Shapes of the computed potential surfaces with the optimal f parameters discussed in Refs. 10 and 21. The top part refers to the FT potential, while the bottom part shows the RBN potential.

$$\left[\frac{d^2}{dR^2} + k_{v'j'}^2 - l'(l'+1)/R^2 \right] \Psi_{v'j'l'}^{ujl}(R) - \sum_{v''j''l''} U_{v'j'l',v''j''l''}^J(R) \Psi_{v''j''l''}^{ujl}(R) = 0. \quad (11)$$

The above equations result from expanding the total wave function of the system in terms of eigenfunctions $\mathcal{Y}_{jl}^{JM}(\Omega_R, \Omega_r)$ of the total angular momentum operator²⁴ and of the vibrational wave functions of the isolated target. The quantities that appear in Eq. (11) are the usual quantities from the conventional notation:²³ $k_{v'j'}$ is the wave number for the $(v'j')$ th rovibrational channel associated with the radial wave function $\Psi_{v'j'l'}(R)$. J and l' are the total and orbital angular momentum quantum numbers, respectively. The indices (vj) define the system state in the incoming channel and the coupling terms $U_{v'j'l',v''j''l''}^J(R)$ are the radial matrix elements of the potential energy surface (multiplied by $2\mu/\hbar^2$) between the angular functions $\mathcal{Y}_{jl}^{JM}$ and $\mathcal{Y}_{j'l'}^{JM}$ and the vibrational wave functions of the diatomic target $\chi_{v'}(r)$ and $\chi_{v''}(r)$. Obviously, there is a different set of coupled differential equations of the form (11) for every value of the total angular momentum J .

The corresponding differential and integral, vibrationally and rotationally inelastic cross sections which are of interest here may be obtained from the corresponding T -matrix elements yielded by the usual asymptotic boundary conditions

$$\begin{aligned} \Psi_{v'j'l'}^{ujl}(R) &\sim \sin(k_{v'j'}R - l'\pi/2) \delta_{vv'} \delta_{jj'} \delta_{ll'} \\ &- (T_{v'j'l',vj'l}^J/2i) \cdot (k_{vj}/k_{v'j'})^{1/2} \\ &\times \exp[i(k_{v'j'}R - l'\pi/2)]; \end{aligned} \quad (12)$$

hence one can write down²³

$$\begin{aligned} \frac{d\sigma}{d\Omega}(vm_j \rightarrow v'j'm_{j'}) &= \left(\frac{1}{4k_{vj}^2} \right) \left| \sum_J (2J+1) \left[\sum_{l'l'} i^{l-l'} (j'm_j J - m_{j'} | j'l'l') \right] \right. \\ &\times \left. T_{v'j'l',vj'l}^J \cdot (jm_j J - m_{j'} | j'l'l') \right] \mathcal{D}_{m_j, m_{j'}}^J(\vartheta) \Big|^2; \end{aligned} \quad (13)$$

where $\mathcal{D}_{m_j, m_{j'}}^J(\vartheta)$ are the angular Wigner functions.²³

The corresponding partial integral cross sections, averaged over initial m_j and summed over final $m_{j'}$ states, are given by

$$\sigma(vj \rightarrow v'j'|E) = \left[\frac{\pi}{k_{vj}^2} (2j+1) \right] \sum_J (2J+1) \sum_{l'l'} |T_{v'j'l',vj'l}^J|^2. \quad (14)$$

Whenever both rotational and vibrational channels are open, then the number of coupled equations increases rapidly beyond the capability of current computing facilities, especially if calculations need to be carried out at several collision energies. One may then try to formulate the problem by taking advantage of various simplifications that could markedly reduce the dimensions of Eq. (11) while still including the basic physical mechanisms for the energy transfer processes.

In the following, we will outline briefly the possible decoupling pathways that may be applied to the system at hand and we will show how the basic element of distinction comes from the comparison of the different time scales associated with the internal motions in the diatomics and with the relative translation, i.e., the actual collision time under the action of the potential field. In the experiments of Ref. 10, the typical vibrational period of the Li_2 molecule was about 0.1 ps, whereas the interaction time τ_{coll} was estimated to be ≈ 0.5 ps. Hence, $\tau_{\text{coll}} > \tau_{\text{vib}}$. Moreover, the rotational period of the same target molecule (say, with $j = 10$) is about 2.0 ps and therefore one also has that $\tau_{\text{coll}} < \tau_{\text{rot}}$, a condition which also allows us to simplify the dynamical treatment.

A. The vibrationally diabatic (VD) dynamics

As mentioned above, if the vibrational motion is fast when compared with the interaction time of the collision partners, then the molecule is effectively vibrating several times as the projectile crosses the range of action of the potential surface. Consequently, the latter atom experiences a molecular target with an averaged internuclear distance that depends on the specific vibrational state of the molecule. In cases where the excitation process is not very efficient, one may consider the averaging to be carried out over the initial vibrational state of the target only

$$\langle \chi_v(r) | V(R, r, \hat{R} \cdot \hat{r}) | \chi_v(r) \rangle = V_{vv}(R, \hat{R} \cdot \hat{r}), \quad (15)$$

hence, $V_v(R, \hat{r} \cdot \hat{R})$ would correspond to a convolution over one particular vibrational state only.

The corresponding coupling matrix elements of Eq. (11) therefore become

$$U_{v'j'l',vj}^J(R) \simeq U_{j'l',jl}^{J,v}(R) \cdot \delta_{vv'} \\ = \int d\hat{r} d\hat{R} \mathcal{Y}_{jl}^{JM*}(\hat{r}, \hat{R}) V_v(R, \hat{R} \cdot \hat{r}) \\ \times \mathcal{Y}_{jl}^{JM}(\hat{r}, \hat{R}), \quad (16)$$

which correspond now to the usual coupling potential for the rigid-rotor (RR) problem with a specific choice of the rotational constant B_e as $B_e(v)$, with v being the particular vibrational state considered during the collision.

The relative coupled equations can now be treated by following two different approaches, which depend once more on further considerations about the different time scales of internal and relative motions.

1. The vibrational diabatic-rotational close-coupled (VD-RCC) equations

Following the general formulation, the modified coupling potential could be taken to treat dynamical processes in which rotational motion is strongly affected by the anisotropy of the field of interaction, thereby allowing the projectile to apply an efficient torque to the molecule during the collision time. The correct way to treat the quantum dynamics is therefore given by the close-coupled (CC) expansion over rotational states

$$\left[\frac{d^2}{dR^2} + k_j^2 - l'(l' + 1)/R^2 \right] u_{jl'l'}^{Jv}(R) \\ = \sum_{j'l'} U_{j'l',j'l'}^{Jv}(R) u_{jl'l'}^{Jv}(R). \quad (17)$$

The above equations could then be called vibrational diabatic-rotational close-coupled (VD-RCC) equations. It should be noted that the potential convolution over vibrational states is called a vibrational diabatic approximation²⁵ to emphasize the fact that the ensuing effective interaction only depends on the asymptotic vibrational state of the target that is used to label the remaining dynamics. Since in collision problems one often employs the adiabatic idea to separate some fast variables from the slow ones,²⁶ then one may say that both rotational and translational motions are considered here as being slower than the vibrational motion of the target. The function of the latter degree of freedom is thus simply that of providing an effective potential from which scattering amplitudes are computed and the corresponding vibrational wave functions are only causing a "geometric" modification of the shape of the RR potential surface, but their relative motion is completely decoupled (diabatic) from the rotational and translational motions.

2. The vibrational diabatic-rotational infinite order sudden (VD-RIOS) equations

In the previous examination of the time scales, we have also pointed out that, in the experiments we wish to analyze, the rotational period of the target molecule τ_{rot} is considered to be markedly larger than the corresponding collision time. This result allows one to further simplify the dynamics and to write down the coupled equations as being parametrically

dependent on the relative orientation $\gamma = \arccos(\hat{R} \cdot \hat{r})$,

$$\left[\frac{d^2}{dR^2} - l'(l' + 1)/R^2 + k_j^2 \right] \mathcal{Y}_{jl}^{l'v}(R; \gamma) \\ = U^{l'v}(R; \gamma) \mathcal{Y}_{jl}^{l'v}(R; \gamma), \quad (18)$$

where both the coupling potential and the continuum wave function now depend on the relative orientation in the body-fixed (BF) frame, on the decoupled angular momentum (translational) l' , and on the fixed wave vector k_j , where j represents the reference rotational state of the target.²³ The corresponding SF T matrix is now given by a convolution over spherical harmonics which represent the target rotational states

$$T_{j-l',j'}^{l'v} = 2\pi(2l' + 1) \int Y_{m_j}^j(\gamma, 0) T_j^{l'v}(\gamma) P_{l'}(\cos \vartheta) \\ \times Y_{m'}^{j'}(\gamma, 0) d \cos \gamma, \quad (19)$$

where ϑ is the SF polar angle for the collision coordinate $R = (\vartheta, \varphi)$. The angular momentum l' here represents the final angular momentum after collision.²³

Equation (18) can be called the vibrational diabatic-rotational infinite order sudden (VD-RIOS) decoupled equation. It is a simplified equation that has already been used to treat the quantum dynamics.^{10,19} We will see below a comparison between different infinite order sudden approximation (IOSA) treatments when computing total integral cross sections at the collision energy of the experiments.

B. The vibrational-rotational infinite order sudden (VR-IOS) cross sections

It is interesting to note at this point that the convolution of Eq. (19) could also be applied to treat a situation in which both the vibrational *and* rotational motions can be considered to be slower than the interaction times. This is obviously the case which corresponds to the other extreme with respect to the one dealt with in the VD approximation, a case where the dynamics is treated by also keeping r as a parameter included in the T matrix of Eq. (19), which would now become dependent on both the r and γ values selected in each calculation

$$T_{vj,v'j'}^{l'v} = 2\pi(2l' + 1) \int \int \chi_v^*(r) Y_{m_j}^{j*}(\gamma, 0) T_j^{l'v}(r; \gamma) \\ \times \chi_{v'}(r) Y_{m_{j'}}^{j'}(\gamma, 0) dr d \cos \gamma. \quad (20)$$

The above T matrix could then be called the VR-IOS approximate T matrix and the corresponding partial differential cross sections will be given by the following equation:

$$\frac{d\sigma}{d\Omega}(vj, v'j' | E) \propto \sum_{l,l'} |T_{vj,v'j'}^{l'v} \cdot T_{vj,v'j'}^{l'v}|^2, \quad (21)$$

which allows for interference structures originating from both the partial wave sums and the different r values employed in each vibrational integral.⁷ In other areas of molecular collisions, the convolution (20) is often called a type of adiabatic approximation.²³

C. The vibrationally close-coupled (VCC) dynamics

In the majority of experimental situations one is faced with the more difficult problem of treating the quantum dy-

namics where interaction time and vibrational periods become comparable $\tau_{\text{vib}} \approx \tau_{\text{coll}}$, and therefore the expansion over vibrational states implied by Eq. (11) needs to be used. Unless one is considering very highly excited rotational states, however, the rotational motion could still be considered as slower than both other motions and therefore may be decoupled from them when solving the scattering equations.

1. The vibrational close-coupled-rotational IOS (VCC-RIOS) equations

The previous paragraphs have discussed the ways in which one can take advantage of the slower rotational motion with respect to interaction times and therefore treats the quantum dynamics for rotationally inelastic processes only at fixed relative orientations of the atom-diatomics system.^{23,27} This approximation handles the coupling between rotational and translational motion within the IOS scheme mentioned before and solves differential equations which depend on the angle γ and which are coupled only through that part of the interaction potential which depends on the vibrational motion

$$\left[\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} + k_v^2 \right] \mathcal{F}_{vv'}^L(R; \gamma) = \sum_{v''} U_{vv''}^L(R; \gamma) \mathcal{F}_{vv''}^L(R; \gamma). \quad (22)$$

They are called here the VCC-RIOS quantum scattering equations. The index L corresponds to the fixed value of the angular momentum (translational) l' defined before and the coupling matrix elements involve the vibrational wave functions of the isolated diatomics

$$U_{vv'}^L(R; \gamma) = \frac{2\mu}{\hbar^2} \int_0^\infty dr \chi_v^*(r) V(R, r, \gamma) \chi_{v'}(r). \quad (23)$$

Solving the above equations for a specific angle γ naturally yields the vibrational S matrix $S_{vv'}(\gamma)$ which parametrically depends on the chosen orientation. The corresponding roto-vibrational S matrix is in turn obtained by convolution over the rotational functions

$$S_{m_j}^L(vj, v'j') = 2\pi \int_0^\pi d\cos\gamma Y_{m_j}^{j' *}(\gamma, 0) S_{vv'}^L(\gamma) \times Y_{m_j}^j(\gamma, 0); \quad (24a)$$

this last quantity can then be used to yield the VCC-RIOS, space-fixed (SF) S matrix $S^J(vj, v'j', l')$,²³ or the SF T -matrix elements

$$T_{m_j}^{l'}(vj, v'j') = 2\pi \int_0^\pi d\cos\gamma Y_{m_j}^{j' *}(\gamma, 0) \times [\delta_{vv'} \delta_{jj'} - S_{vv'}^{l'}(\gamma)] Y_{m_j}^j(\gamma, 0), \quad (24b)$$

where the identification $L = l'$ has been used to perform the transformation.²⁸ The degeneracy-averaged VCC-RIOS partial differential cross sections are then given by

$$\frac{d\sigma}{d\Omega}(vj, v'j' | \Omega) = \frac{1}{4(2j+1)k_v^2} \sum_{m_j=-m_*}^{m_*} \left| \sum_{l'} (2l'+1) \times |T_{m_j}^{l'}(vj, v'j') P_{l'}(\cos\vartheta)|^2 \right|, \quad (25)$$

where the angle ϑ has already been defined in Eq. (19). Here $m_* = \min(j, j')$. The corresponding partial opacities are given by

$$\sigma'(vj, v'j' | E) = \frac{\pi(2l'+1)}{(2j+1)k_v^2} \sum_{m_j=-m_*}^{m_*} |T_{m_j}^{l'}(vj, v'j')|^2 \quad (26)$$

and the partial integral cross sections are

$$\sigma(vj, v'j' | E) = \sum_{l'} \sigma'(vj, v'j' | E). \quad (27)$$

It is interesting to note at this point that if one expands the argument of the integral on the right-hand side of Eq. (24) in the following way:

$$[\delta_{vv'} - S_{vv'}^{l'}(\gamma)] = T_{vv'}^{l'}(\gamma) = \sum_{\lambda} A_{\lambda}^{l'}(v, v') P_{\lambda}(\cos\gamma), \quad (28)$$

then one can obtain the following special opacity:

$$\sigma^{\lambda}(v, v') = \frac{\pi}{k_v^2} \sum_{l'} (2l'+1) |A_{\lambda}^{l'}(v, v')|^2, \quad (29)$$

and define with its aid the state-to-state rotovibrational cross sections²⁹

$$\sigma(vj, v'j' | E) = \sum_{\lambda} \frac{1}{2\lambda+1} C^2(j\lambda j' | 000) \sigma^{\lambda}(v, v') \quad (30)$$

and the rotationally summed, vibrationally inelastic partial cross sections

$$\sigma(v, v' | E) = \sum_{\lambda} \frac{1}{2\lambda+1} \sigma^{\lambda}(v, v'). \quad (31)$$

This means, as is well known, that the entire matrix of the rotational-vibrational inelastic transition is given via the weighted sum of the fewer elements as defined by Eq. (30).

2. The vibrational distorted wave rotational infinite order sudden (VDW-RIOS) equations

In situations where we expect the vibrational inelasticity to be rather small, then one can further simplify the form of Eq. (22) and start by solving the vibrationally elastic problem first

$$\left[\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} + k_v^2 \right] \mathcal{F}_{vv'}^L(R; \gamma) = U_{vv'}^L(R; \gamma) \mathcal{F}_{vv'}^L(R; \gamma). \quad (32)$$

One then constructs the inelastic (off-diagonal) terms of the corresponding T matrix by simply using the separate elastic solutions and couple them with the required potential function *after* the elastic dynamics has been solved³⁰

$$T_{v'v''}^{l'}(\gamma) = \frac{1}{(k_v^2 k_{v''}^2)^{1/2}} \int_0^\infty \mathcal{F}_{vv''}^{l'}(R; \gamma) U_{v'v''}^{l'}(R; \gamma) \times \mathcal{F}_{v'v''}^{l'}(R; \gamma) dR. \quad (33)$$

The above approximation produces the vibrational distorted wave and rotational IOS (VDW-RIOS) T -matrix elements that can then be employed directly into the equations for the partial differential and integral cross sections mentioned before.

The various decoupled solutions of the quantum scatter-

ing problem that have been discussed and presented in this section are meant to provide a set of different computational procedures which can be tested directly for the present atom-diatomics system, taking advantage of the fact that the two model potential surfaces suggested for it in the literature are both explicitly including the dependence on the vibrational coordinate.

The results of the computations and their comparison with available experiments will be analyzed in the following section.

IV. RESULTS AND DISCUSSION

As already mentioned in the Introduction, the only calculations carried out earlier were performed within the VD-RIOS approximation discussed in the previous section^{10,21} and employed both the FT and the RBN potential functions. In order to better understand the relative role of the various decoupling approximations, we have carried out an extensive range of computations, using again both potential functions, employing all the approximations discussed before. A comparison of some of the various results with both PES is shown in Table I. The calculations were carried out at a collision energy of 80 meV and the integral cross sections shown correspond to the rotationally summed values or to the rotationally *and* vibrationally summed values, depending on the employed decoupling scheme. The integrations employed were all variations of a Numerov propagator²³ and asymptotic matching was carried out at distances where the PES were less than 10^{-6} a.u. Convergence on partial wave expansion, rotational and/or vibrational channel expansion, and closed-channel inclusion were all tested in order to ensure stabilization of the individual cross sections within $\approx 2\%$ of their values. The vibrational wave functions of the Li_2 molecule were obtained by numerical integration

using the analytic potential of the target as given in the experimental papers.¹⁰ The corresponding coupled matrix elements needed in the VCC-RIOS approximation were also obtained by numerical integration at all the R and γ values required to obtain the continuum solutions. The number of γ values in the IOS quadrature was increased up to 20 in the $(0, \pi/2)$ quadrant, although 10–15 points were usually sufficient for convergence in a Gauss quadrature.

An examination of the results shown in the table allows one to make the following observations:

(i) The PES used here for the Li_2 -He system appear to exhibit a rather weak vibrational coupling, since the VCC and VDW treatments produce remarkably similar results across the whole range of v values and down to the fourth significant figure. It follows also from the present results that both potential functions include vibrational coupling in a similar fashion, hence this closeness of the VCC and VDW results shown by the FT and RBN calculations.

(ii) The approximate treatment of the rotational dynamics employed in the previous calculations^{10,19} using the VD-RIOS approach is obviously missing part of the physics involved since, when the rotational coupling is included correctly, both potential functions give very different results. For the $v = 0$ situation, the VD calculations with either the RIOS or the RCC approach are very close to each other for the RBN surface and not very different from each other in the case of the FT potential. As v increases, however, the effect of correspondingly increasing the angular anisotropy of each potential produces dramatic differences with the RBN function, while the effect is less dramatic for the FT potential. In both cases, however, the correct CC treatment of rotational coupling markedly modifies the final total cross sections.

(iii) When the diabatic assumption is removed for the vibrational motion and the calculations are carried out with-

TABLE I. Computed total cross sections (rotationally and vibrationally summed) for $\text{He-Li}_2(X^1\Sigma_g^+)$ using the different dynamical approximations defined in the main text. All quantities are in atomic units. The collision energy was 80 meV.

RBN($f = -0.5$)	VD-RIOS ^a	VD-RCC	VCC-RIOS	VDW-RIOS
$v = 0$	642.2	644.07	644.86	644.37
2		647.33	647.83	647.33
3		648.83	649.17	648.85
4		650.28	650.43	650.42
7		654.55	654.25	654.31
10		659.42	658.73	658.81
15		670.17	666.21	666.03
20	607.7	681.20	673.40	673.03
FT($f = +2$)	VC-RIOS ^b	VD-RCC	VCC-RIOS	VDW-RIOS
$v = 0$	562.2	582.51	588.50	588.30
2		571.99	592.90	592.99
3		568.18	595.59	595.55
4	≈ 510.0	565.10	598.54	598.34
7		558.62	609.03	609.65
10		559.44	621.17	622.46
15		590.44	648.90	650.16
20	618.7	623.49	685.32	680.93

^a From Ref. 19.

^b From Ref. 10.

in the VCC model for that coupling, then results change quite markedly for both potentials as the target vibrational content increases. This means that in spite of the rovibrational coupling being weak for both PES, the total integral cross sections exhibit a strongly altered dependence on the v index and, in the case of the FT potential, the VCC-RIOS results differ from the VD-RIOS model by up to more than 10% by the time $v = 20$.

It is also interesting to note that the three different dynamical coupling models employed in the present work (VD-RCC, VCC-RIOS, VDW-RIOS) correspond to three very different numerical codes that employ the same two PES discussed here and therefore could be used to check their numerical quality against each other. The fact that all the $v = 0$ results turn out to be, for both systems, so close to each other is direct evidence of the reliability of our calculations.

The experimental results¹⁰ of the present system have shown the following features of the general behavior of total integral (rotationally and vibrationally summed) cross sections as a function of the mean internuclear distance $\langle r \rangle_v$ (or of the target vibrational quantum number):

(i) the cross sections decreased as v increased from $v = 0$ up to $\approx v = 6$ by about 10% of their initial values;

(ii) they then began to increase up to $\approx v = 20$, reaching a maximum value of about 12% more than their $v = 0$ value, showing a steady behavior after the "dip" for $v = 6$;

(iii) the experimental energy was ≈ 78 meV and the quality of the data was considered to be better for the low- v measurements, increasing the error bars as v increased up to $\approx 30\%$. This uncertainty will be reflected in our analysis of the computation.

We used the present computational models to study the experimental behavior and to see if one could attribute it to specific features of either the dynamics or the interaction potential.

For both the PES employed, we ran calculations with various values of the f parameters and found the following:

(i) The RBN potential never exhibited any decrease of computed cross sections as v increased for any of the selected values of f . By keeping f negative we made sure that the PES maintained a DM behavior, while positive f values corresponded to ADM behavior that was considered to be physically unrealistic and certainly at variance with the FT behavior.

(ii) The value of $f = -0.5$, suggested previously²² for the RBN surface, was also used here to produce the results of Table I. None of the cross sections exhibits any minimum feature as a function of v .

(iii) The calculations with the FT surface were carried out with all three decoupling schemes. Only the VD-RCC approach showed agreement with experimental findings. The behavior of the above calculations, as a function of different f values, is shown in Fig. 4 over the same range of v values examined by the experiments.¹⁰

As mentioned before, the larger f values correspond to more anisotropic potential functions. The results from our computed percentage variations show that only for f values around $f = 2$ and $f = 3$, the calculations begin to reproduce

FIG. 4. The relative integral cross section (%) computed with the VD-RCC approximation discussed in the main text and using the FT potential of Ref. 10. Φ are the experimental points of Ref. 10. The various curves indicate the behavior of the $(\sigma_v - \sigma_0)/\sigma_0$ as a function of v and of the f parameter in the potential surface. Each f value for each curve is given at the extreme right of the figure, e.g., the dashed curve corresponds to $f = 3$. The top two values of f correspond to negative parameters.

experimental findings and indicate the presence of a dip around $v \approx 6$. As the vibrational coupling is introduced, however, the effect disappears and the VCC-RIOS calculations show no minimum in their v dependence.

It is interesting to probe further the behavior of the computed cross sections and therefore to see how the different, partial contributions behave as a function of the vibrational content of the target molecule. This partitioning is shown for the cross sections via the FT potential in Fig. 5 and for the RBN potential in Fig. 6.

The results via the FT potential report two sets of results from the VD-RCC calculations. The elastic part of the total integral cross sections σ_{el}^{rot} marked by crosses and the inelastic part σ_{inel}^{rot} marked by open circles defined in the scale on the right-hand side of the figure. One sees clearly that the inelastic, rotationally summed contributions increase as expected as v increases and constitute only $\approx 30\%$ of the total cross sections. The elastic part, on the other hand, shows a marked dip around $v \approx 10$ and exhibits a general behavior which determines the total cross section behavior of Fig. 4.

As the vibrational motion is coupled with rotations, however, the whole picture changes, as shown by the elastic and inelastic partial cross sections from the VCC-RIOS calculations (open squares and filled circles, respectively, in Fig. 5). The vibrationally elastic contributions are already including rotationally summed cross sections, a fact which explains their larger values than before. They, however, de-

FIG. 5. Computed elastic and inelastic integral cross sections via the FT potential of Ref. 10. The results with the VD-RCC model are given by crosses (σ_{el}^{rot}) and by open circles (σ_{inel}^{rot}), while the results with the VCC-RIOS quantum approach are given by open squares (σ_{el}^{vibrot}) and by filled circles (σ_{inel}^{vibrot}). All quantities are in atomic units. The scale on the left-hand side refers to the elastic contributions, while the one on the right-hand side refers to the inelastic contributions. The various symbols listed above are connected in the figure by different lines in order to aid the eye to view each overall behavior.

crease with increasing ν values and show no minimum because of the much stronger dependence of the inelastic part on the ν index. The vibrational coupling is now increasing the overall flux into the inelastic channels and produces larger cross sections as the molecular vibrational content increases. As a result, the elastic part can only decrease with increasing ν values.

The calculations performed using the RBN potential surface are summarized in Fig. 6 and present quite a different picture for their partial contributions. Within the VD-RCC model, one now sees that the rotationally inelastic part (open circles) is slightly smaller than that of the FT potential, but varies more markedly with ν (about a 50% variation vs $\approx 30\%$ in the earlier case). The elastic cross sections, on the other hand, are larger for the RBN potential and do not manage to present a minimum because of the greater flux diversion into inelastic channels as ν increases.

From the comparison of the two potentials within the

FIG. 6. The same as in Fig. 5, but for the calculations performed via the RBN potential discussed in the main text.

VD-RCC model, therefore, it appears that the FT potential exhibits a larger angular anisotropy as ν increases and a smaller target "size" for larger ν values than the RBN function. As a consequence, the RBN potential shows smaller rotational inelasticity, but larger elastic cross sections thus preventing its total cross sections from reproducing an experimental minimum. Because of the greater relative importance of inelastic effects in its cross sections, the FT potential is instead capable of reproducing the experimental findings due to the interplay between elastic scattering and rotationally inelastic channels as ν increases.

The effect of the target vibrational content is also taken into account within the VCC-RIOS model of the dynamics. In this case, however, the vibrational motion is, more correctly, coupled to the translational motion *during* the dynamical evolution of the collision partners. One therefore sees that the relative fluxes into the various rovibrational channels are now rather different for the RBN potential, as was before the case with the FT results of Fig. 5. The results of Fig. 6, in fact, show that the vibrationally elastic (rotationally summed) cross sections from the RBN potential (open squares) are larger than the same results with the FT potentials and vary very little with the ν index. On the other hand, the vibrationally inelastic part (filled circles) is about ten times smaller than that of the FT calculations (Fig. 5) and increases only in the region of very large ν values. No minimum therefore can appear in the corresponding total cross sections as a function of ν values.

The vibrational coupling in the RBN PES therefore turns out to be markedly weaker than that in the FT potential, while the size of the target is much larger in the former potential than in the latter. Moreover, the relative rotational anisotropies are also fairly different, with the FT potential being more anisotropic for each ν value.

One convenient way of defining such anisotropy is simply given by the value $|\Delta R|$ of the differences between classical turning points at the given collision energy.^{31,32} This positive quantity, defined as $|\Delta R| = R_{||} - R_{\perp}$, has been shown to be related to the efficiency with which translational motion is coupled to the rotational states of the target, thereby allowing the rotationally inelastic processes to occur during the collision.^{31,32} The behavior of such a quantity, as a function of the target vibrational index ν , is shown in Fig. 7 for both potential functions; one sees clearly that the FT surface is more anisotropic than the RBN surface and is more so for the lower ν values. As the f parameter is varied, one also observes (see the inset in Fig. 7) that the ΔR values goes through a minimum around $\nu \approx 4$, hence suggesting that the elastic cross section minimum of Fig. 5 should be related to the anisotropy features of that surface.

Recent calculations³³ have produced an alternative analytic expression for the He-Li₂ interaction and we decided to further test it with the present dynamical models. It is worth noting at this point that the more recent potential function, to be called the Varandas (VRDS) surface, exhibits general features which are very close to the previous FT PES, with $|\Delta R|$ values which vary between $1.06a_0$ for $\nu = 0$ and $1.71a_0$ for $\nu = 22$ and which show a rather marked minimum for $\nu \approx 4$ with $|\Delta R| = 0.570a_0$. The corresponding inelastic

FIG. 7. The computed potential anisotropy $|\Delta R|$ in a_0 units as a function of the vibrational state of the target. The values were computed as $|R - R_1|$ at the collision energy of 80 meV and for the VD picture of the interaction. The crosses refer to the FT potential, while the filled circles are from the RBN potential. The inset shows the behavior of the FT potential around a minimum value of $|\Delta R|$.

cross sections are therefore only slightly larger than those given by the FT potential, when the VD-RCC approach is used, as one can see from the results reported in Table II.

It is also interesting to see from Table II that the more correct inclusion of vibrational coupling within the VCC-RIOS model once more produces results which are very close to those obtained via the FT potential function, a fact confirmed by the VDW-RIOS calculations in the last column of Table II. In conclusion, the VRDS potential appears to be very close to the FT surface in terms of vibrational coupling, but slightly stronger in terms of rotational anisotropy, hence preventing its calculated cross sections to exhibit the minimum value for a specific v index shown by the experiments.

V. CONCLUSIONS

The model calculations employed to test the effects of vibrational and rotational coupling in He-Li₂ collisions have shown the following:

(i) The minimum value shown by the total cross sections as a function of the vibrational quantum number should be attributed mostly to the elastic part of the collision that is being modified by the changing size of the target molecule as v increases.

(ii) The changing anisotropy of the potential (as v increases) modified the “shape” of the ellipsoid of interaction which in turn controls the amount of flux going into rotational inelasticity. If the latter becomes too large, its increase with v cancels the possible minimum effect in the total cross sections. This is the case with the RBN and VRDS potentials, while the FT surface appears to be the most realistic on this account.

(iii) The explicit inclusion of vibrational coupling during the dynamics appears to cancel the minimum, producing larger total cross sections which always increase with v . In these calculations, however, rotational coupling is only included approximately via the IOS model and therefore their less rigorous treatment of rotational inelasticity, as opposed to the VD-RCC calculations, may also be the cause of this discrepancy. When observing the results displayed in Figs. 5 and 6, one notices that in the low- v region, the rotational inelasticity is smaller than in the high- v region and therefore, as v increases, it becomes a larger fraction of the elastic cross section for both potential functions. This fact may suggest that the IOS portion of the VCC-RIOS calculations possibly fares less realistically as the target becomes more vibrationally excited, thus masking the minimum feature shown by the VD-RCC calculations of Fig. 4. The latter model, on the other hand, treats correctly the interference and coupling factors in the quantum dynamics of rotations and only suggests that vibrations occur on a faster time scale. It therefore appears that all the examined potential functions have a rather strong coupling between vibration-rotation and relative motions and therefore require all a rigorous treatment of their relative dynamics in order to unequivocally assess their quality from specific experiments.

(iv) Rotational excitations are reasonably well described by the IOS decoupling in qualitative terms, while quantitative agreement with experiments (e.g., appearance of the minimum in the cross sections) necessarily requires close coupling calculations as shown by our results of Fig. 4.

(v) The interaction between vibrational and translational motion in the present system appears to be rather weak, as shown by a comparison between VCC and VDW results with all potential functions. However, the coupling between rotations and vibrations during collisions requires rather careful handling for quantitative agreement to be reached and may not be given realistically by dimensionality reductions based on time scale consideration of ground vibrational states of targets as is the case in the VCC-RIOS approach.

TABLE II. The same calculations as in Table I, but using the VRDS potential of Ref. 33. The units and the meaning of the symbols are the same as in the previous table.

	VD-RCC	VCC-RIOS	VDW-RIOS
$v = 0$	581.92	582.17	582.26
2		591.70	591.91
3		596.97	597.37
4	594.76	602.57	602.95
7		617.05	616.91
10		628.19	628.20
15	632.22	647.27	647.10
20		666.43	666.02

VI. ACKNOWLEDGMENTS

We are grateful to the Italian National Research Council for the financial support and to the IBM 3090-600 J of the NIC-CASPUR project at the University of Rome which has made the present calculations possible. We are also grateful to the Italy-Spain Intensive Action collaborative program which allowed several visits between research groups during the period in which this work was completed. S.S. is also grateful to the IBM ECSEC Center in Rome for a Visiting Fellowship in 1991. Finally, we wish to thank Professor Var-

andas and Dr. Rubhan for letting us have some of their results prior to publication.

- ¹See, e.g., J. P. Toennies, *Annu. Rev. Phys. Chem.* **27**, 225 (1976).
²M. Faubel, *Adv. At. Mol. Phys.* **19**, 345 (1983).
³H. H. Dispert, M. W. Geis, and P. R. Brooks, *J. Chem. Phys.* **70**, 5317 (1979).
⁴Z. Kary and R. N. Zare, *J. Chem. Phys.* **68**, 3360 (1978).
⁵R. B. Bernstein, *Chemical Dynamics via Molecular Beam and laser techniques* (Oxford University, New York, 1982).
⁶H. J. Loesch, M. Hoffmeister, and F. Stienkemeier, *J. Chem. Soc. Faraday Trans.* **285**, 1052 (1989).
⁷H.-G. Rubhan and K. Bergmann, *Annu. Rev. Phys. Chem.* **41**, 735 (1990).
⁸K. T. Tang and J. P. Toennies, *J. Chem. Phys.* **76**, 2424 (1977).
⁹E. Gottwald, A. Mattheus, and K. Bergmann, *J. Chem. Phys.* **86**, 2680 (1987).
¹⁰M. Fuchs and J. P. Toennies, *J. Chem. Phys.* **85**, 7062 (1986).
¹¹H.-G. Rubhan and J. P. Toennies, *J. Chem. Phys.* **89**, 287 (1988).
¹²H.-G. Rubhan, N. Sathyamurthy, and J. P. Toennies, *Faraday Discuss. Chem. Soc.* **84**, 356 (1987).
¹³H.-G. Rubhan and J. P. Toennies, *Chem. Phys.* **126**, 7 (1988).
¹⁴U. Stahal, diploma thesis, University of Bochum, Bochum, Germany, 1983.
¹⁵W. Müller and W. Meyer, *J. Chem. Phys.* **85**, 953 (1986).
¹⁶D. Rapp and T. Kassal, *Chem. Rev.* **69**, 61 (1969).
¹⁷T. F. George and J. Ross, *Annu. Rev. Phys. Chem.* **24**, 37 (1973).
¹⁸D. Secrest, *Annu. Rev. Phys. Chem.* **24**, 137 (1973).
¹⁹H.-G. Rubhan, *J. Chem. Phys.* **92**, 5384 (1990).
²⁰K. T. Tang and J. P. Toennies, *J. Chem. Phys.* **80**, 3726 (1984).
²¹H.-G. Rubhan and N. Sathyamurthy, *Chem. Phys. Lett.* **171**, 506 (1990).
²²H.-G. Rubhan (private communication).
²³See, e.g., F. A. Gianturco *The Transfer of Molecular Energy by Collisions* (Springer, Berlin, 1979).
²⁴A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. London, Ser. A* **256**, 540 (1969).
²⁵M. M. Marica, *Chem. Phys.* **100**, 203 (1985).
²⁶F. A. Gianturco, G. Delgado-Barrio, O. Roncero, and P. Villareal, *Mol. Phys.* **71**, 1405 (1990).
²⁷R. T. Pack, *J. Chem. Phys.* **60**, 633 (1974).
²⁸P. McGuire and D. J. Kouri, *J. Chem. Phys.* **60**, 2488 (1974).
²⁹R. Goldflam, S. Green, and D. J. Kouri, *J. Chem. Phys.* **67**, 225 (1977).
³⁰L. Eno and G. G. Balint-Kurti, *Chem. Phys.* **23**, 295 (1977).
³¹F. A. Gianturco, J. P. Toennies, M. Bernardi, and M. Venanzi, *J. Chem. Phys.* **93**, 2437 (1990).
³²F. A. Gianturco, M. Bernardi, and J. P. Toennies, *J. Chem. Soc. Faraday Trans.* **87**, 31 (1991).
³³A. J. C. Varandas (private communication).