Photofragmentation of the NiCl complex: A three-dimensional quantum mechanical study

O. Roncero, J. A. Beswick, N. Halberstadt, P. Villarreal, and G. DelgadoBarrio

Citation: *J. Chem. Phys.* **92**, 3348 (1990); doi: 10.1063/1.458578

View online: <http://dx.doi.org/10.1063/1.458578>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v92/i6>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis

- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics

- plasma source characterization
- etch and deposition process
- reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue

Photofragmentation of the Ne...ICl complex: A three-dimensional quantum mechanical study

O. Roncero^{a)} and J. A. Beswick
LURE,^{b)} Université de Paris Sud, 91405 Orsay, France

N. Halberstadt
Laboratoire de Photophysique Moléculaire,^{c)} Université de Paris Sud, 91405 Orsay, France

P. Villarreal and G. Delgado-Barrio
Instituto de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain

(Received 3 August 1989; accepted 7 November 1989)

Converged three-dimensional quantum mechanical calculations for photofragmentation of the Ne...ICl van der Waals molecule in the energy region of the electronically excited $B(^3\Pi_{0-})$ state of ICl are presented and compared with experiments. Lifetimes and final state distributions for the ICl fragments were determined for vibrational predissociation from the lowest van der Waals level in the $B(v' = 2)$ channel. Good agreement between theory and experiment was achieved using a sum of atom-atom pairwise potentials. This potential energy surface predicts the equilibrium geometry of the complex to be bent at 140° with the Ne atom towards the Cl end of ICl. The diabatic vibrational golden rule (DVGR) approximation, as well as the rotational infinite order sudden approximation (RIOS), have been tested against the full 3D calculations. Analysis of the quasibound wave function reveals that the highly inverted rotational distribution of the ICl fragments observed in the experiment, is not due to zero-point bending motion. It is more likely to be due to a rotational rainbow effect enhanced by the favorable initial geometry of the complex. The effect of the excitation of the bending van der Waals mode in the complex has also been studied. As compared with the lowest level, a longer lifetime and a different rotational distribution of the fragments is predicted. The results presented in this work not only elucidates many dynamical aspects of vibrational predissociation for the Ne...ICl complex, but also provide benchmark data for the study of other theoretical methods and approximations.

I. INTRODUCTION

Photofragmentation studies in van der Waals and hydrogen-bonded complexes provide central information on intermolecular forces as well as on intramolecular energy transfer and redistribution polyatomic systems. Lately,¹ several experimental studies have been conducted in electronically excited states of triatomic systems involving a rare gas atom and a halogen or a interhalogen diatomic molecule. These experiments provided a wealth of detailed information on the dynamics of vibrational predissociation processes: lifetimes and linewidths, spectral shifts, as well as final state vibrational and rotational distributions of the diatomic fragment. A variety of dynamical effects were reported:

- (1) Propensity rules and superlinear dependence of the vibrational predissociation rates on the initial vibrational excitation.
- (2) Rainbow and interference effects in the final rotational distribution of the fragments.
- (3) Intramolecular vibrational redistribution prior to dissociation.

From the theoretical point of view, three dimensional quantum mechanical calculations have been conducted for

the $Rg\cdots Cl_2$ ($Rg = He, Ne, Ar$) systems.²⁻⁵ From these calculations the following conclusions have emerged:

- (1) A sum of pairwise atom-atom potentials was able to fit lifetimes as well as final state distributions.
- (2) The diabatic vibrational golden rule (DVGR) and the rotational infinite order sudden approximation (RIOS) gave usually very good results.
- (3) The coupling between rotational and translational degrees of freedom in the final vibrational state was crucial in determining the final rotational state distribution.

It is important to extend these theoretical studies to other systems in order to assess the general validity of these conclusions. In particular the rare gas-interhalogen systems are very interesting in that, not having the homonuclear symmetry, they show new dynamical effects. Recently,⁶ Lester and co-workers have studied the Ne...ICl complex in the region of the $ICl(B^3\Pi_{0-}, v' = 2)$ excited state. A highly inverted ICl fragment rotational distribution centered at $j \sim 17$ has been found and interpreted as the result of a rotational rainbow effect. It is the purpose of this paper to present a full 3D quantum mechanical study of vibrational predissociation in Ne...ICl(B).

The calculations were performed using a sum of atom-atom pairwise interactions. Good agreement with the experimental final state rotational distribution has been obtained. By comparing the results of the full 3D calculation with a simple decomposition of the initial quasibound wave

^{a)} Permanent address: Inst. Estruct. de la Materia, CSIC, Madrid, Spain.

^{b)} Laboratoire du CNRS, CEA et MEN.

^{c)} Laboratoire du CNRS.

function in terms of free rotor states, it was possible to show that the highly inverted rotational distribution of the ICl fragments is indeed due to the effect of torques during the dissociation. In addition, we have found features in the rotational distribution which are the result of the bent initial geometry of the complex. Finally, since the calculations presented here have been performed with high numerical accuracy, they provide benchmark data which can be used to test other theoretical methods and approximations.

The organization of the paper is the following. In Sec. II we present the general methodology for the quantum mechanical three-dimensional calculations of the photoexcitation cross sections as well as the approximate treatments DVGR and RIOSA. In Sec. III we describe the Ne...ICl system and we define the potential energy surface used in the calculations. Section IV presents the full 3D results, the comparison with the experimental values and the study on the validity of the DVGR and RIOSA calculations. The effect of the initial state of the complex on the vibrational predissociation dynamics is also analyzed. Finally, Sec. V is devoted to the conclusions.

II. METHODOLOGY

In this work we have used the earlier developed method^{2-5,7-9} for line shape calculations based on the following three steps procedure:

- (1) Calculation of the initial bound state wave function by diagonalization in a suitable stretching-bending basis set.
- (2) Calculation of the final dissociative wave function by integration of a set of rovibrational close-coupled equations with respect to the dissociative coordinate.
- (3) Determination of the photofragmentation cross section by calculation of the transition dipole moment matrix elements between the bound and the dissociative wave functions.

In addition to these full 3D calculations, we have also studied the validity of two widely used approximations:

(1) The diabatic vibrational golden rule (DVGR) approximation. In van der Waals systems the coupling between the vibrational motion of the diatomic and the van der Waals stretching and bending vibrations is rather weak. Therefore, the spectrum is usually composed of isolated lines corresponding to excitation of the diatom which are broadened by vibrational predissociation and or rotational predissociation. Under those conditions, the usual golden rule model based on a discrete isolated level facing several continua should be valid.

(2) The rotational infinite order sudden approximation (RIOSA). Another important approximation in the treatment of the couplings between rotational and translational degrees of freedom can be implemented by performing the calculations at several fixed angular orientations of the diatomic molecule, followed by an average over these orientations. This approximation, when applied to the calculation of the final continuum wave functions, gave rather accurate results for the Ne...Cl₂ complex even though the average

kinetic energy was not much larger than the rotational energy of the fragments.⁵ It is thus interesting to check whether this is still true for a system like Ne...ICl for which the rotational excitation is even larger.

In the following we present the general formalism for the full 3D calculation as well as for these two approximate treatments.

A. Full 3D photofragmentation cross sections

In the framework of the first order perturbation theory for electric dipole transitions, the cross section for excitation of a system from an initial bound state $|\Psi_i\rangle$, with energy E_i , to a final continuum state $|\Psi_{fE}\rangle$ with energy E , is given by

$$\sigma_{fE-i} \propto |\langle \Psi_{fE} | \boldsymbol{\mu} \cdot \mathbf{e} | \Psi_i \rangle|^2 \quad \text{with } E = E_i + \hbar\omega, \quad (1)$$

where $\mathbf{e}$ is the polarization vector of the incident photon, with energy $\hbar\omega$, and $\boldsymbol{\mu}$ the transition dipole moment. In the case studied here $|\Psi_i\rangle$ is a discrete rovibrational wave function of the electronic ground state X of the Ne...ICl complex, while $|\Psi_{fE}\rangle$ is the continuum rovibrational wave function for the excited electronic state B .

The wave functions Ψ_i and Ψ_{fE} are solutions of Hamiltonians of the form

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{L^2}{2mR^2} + \frac{j^2}{2\mu r^2} + V_{\text{ICl}}(r) + W(r, R, \theta), \quad (2)$$

where r is the intramolecular distance of ICl, R the distance between Ne and the center of mass of ICl, and θ the angle between the two vectors $\mathbf{r}$ and $\mathbf{R}$, $\theta = 0$ corresponding to the collinear configuration with the neon atom on the iodine side (see Fig. 1). In Eq. (2) $m = m_{\text{Ne}}m_{\text{ICl}}/(m_{\text{Ne}} + m_{\text{ICl}})$ is the reduced mass for the intermolecular motion, $\mu = m_{\text{I}}m_{\text{Cl}}/(m_{\text{I}} + m_{\text{Cl}})$ is the reduced mass for the intramolecular motion, while L and j are the two angular momenta associated to $\mathbf{R}$ and $\mathbf{r}$, respectively. Thus j will be the quantum number associated to the rotation of the ICl fragment. The $V_{\text{ICl}}(r)$ and $W(r, R, \theta)$ functions are the intramolecular (ICl) and van der Waals intermolecular potentials, respectively.

FIG. 1. Contour plots of the intermolecular potential energy surface used in this work for the Ne...ICl(B) van der Waals molecule. The ICl molecule is fixed at its equilibrium internuclear distance. The contour lines are 10 cm⁻¹ apart the outermost being at 10 cm⁻¹ below the dissociation threshold.

We treat differently the initial Ψ_i bound and the final Ψ_{fE} continuum wave functions. For the bound states we expand the wave functions as

$$\Psi_i(\mathbf{r}, \mathbf{R}) = \sum_{v''} \sum_{n''_b, n''_g} a_{v'' n''_b n''_g}^{(i)} \chi_{v''}^{(i)}(r) \chi_{n''_b}^{(i)}(R) \chi_{n''_g}^{(i)}(\hat{r}, \hat{R}), \quad (3)$$

where $\chi_{v''}^{(i)}(r)$ is an intramolecular basis set, taken to be equal to the "free" ICl wave functions obtained by numerical integration of

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V_{\text{ICl}}^{(i)}(r) \right\} \chi_{v''}^{(i)}(r) = E_{v''}^{(i)} \chi_{v''}^{(i)}(r). \quad (4)$$

The $\chi_{n''_b}^{(i)}(R)$ on the other hand, is a harmonic oscillator basis set with frequency and equilibrium distance corresponding to a harmonic fit of the average potential $W_{v_0 v_0}^{(i)}(R, \theta) = \langle \chi_{v_0}^{(i)} | W^{(i)}(r, R, \theta) | \chi_{v_0}^{(i)} \rangle$, for a reference vibrational level v_0 at the equilibrium angular geometry. Finally the $\chi_{n''_g}^{(i)}(\hat{r}, \hat{R})$ is a bending basis set for the $W_{v_0 v_0}^{(i)}(R, \theta)$ potential at the minimum $R = R_0$ of the well, i.e.,

$$\left\{ \frac{l^2}{2mR_0^2} + B_{v_0}^{(i)} \frac{j^2}{\hbar^2} + W_{v_0 v_0}^{(i)}(R_0, \theta) \right\} \chi_{n''_b}^{(i)}(\hat{r}, \hat{R}) = E_{n''_b}^{(i)} \chi_{n''_b}^{(i)}(\hat{r}, \hat{R}) \quad (5)$$

with $B_{v_0}^{(i)}$ being the rotational constant of ICl in the vibrational state v_0 . $E_{n''_b}^{(i)}$ are the energies associated to these "zero-order" bending (or hindered rotor) basis set. To solve Eq. (5), the bending wave functions are further expanded as

$$\chi_{n''_b}^{(i)}(\hat{r}, \hat{R}) = \sum_{j, \Omega} b_{n''_b j \Omega}^{(i)} \Theta_{j \Omega}^{(J, M, p)}(\hat{r}, \hat{R}), \quad (6)$$

where $\Theta_{j \Omega}^{(J, M, p)}(\hat{r}, \hat{R})$ is a free rotor basis set in the body-fixed system of reference¹⁰:

$$\Theta_{j \Omega}^{(J, M, p)}(\hat{r}, \hat{R}) = [2(1 + \delta_{\Omega 0})]^{-1/2} [\Phi_{j \Omega}^{(J, M)}(\hat{r}, \hat{R}) + p(-1)^J \Phi_{j - \Omega}^{(J, M)}(\hat{r}, \hat{R})] \quad (7)$$

with

$$\Phi_{j \Omega}^{(J, M)}(\hat{r}, \hat{R}) = \left[\frac{(2J+1)}{4\pi} \right]^{1/2} \times D_{M \Omega}^{J*}(\varphi_R, \theta_R, 0) Y_{j \Omega}(\theta, \varphi), \quad (8)$$

where J is the quantum number associated to the total angular momentum $\mathbf{J} = \mathbf{l} + \mathbf{j}$, M the projection of $\mathbf{J}$ on the labo-

ratory- z axis, $\Omega > 0$ its projection on the body-fixed axis $\mathbf{R}$, and $p = \pm 1$ the parity under total nuclear coordinates inversion. The $D_{M \Omega}^{J*}(\varphi_R, \theta_R, 0)$ and $Y_{j \Omega}(\theta, \varphi)$ are the Wigner and spherical harmonics rotational functions,¹¹ θ_R and φ_R being the polar angles specifying the direction of the $\mathbf{R}$ vector with respect to the space fixed system, while θ and φ being the polar angles of the $\mathbf{r}$ vector in the body fixed system. In the representation given by Eq. (7) the j^2 operator is diagonal with eigenvalues $\hbar^2 j(j+1)$. The l^2 operator on the other hand has diagonal and nondiagonal matrix elements which can be calculated using

$$\begin{aligned} \langle \Phi_{j \Omega} | l^2 | \Phi_{j' \Omega'} \rangle &= \hbar^2 \delta_{\Omega, \Omega'} [J(J+1) + j(j+1) - 2\Omega^2] \\ &\quad - \hbar^2 \delta_{\Omega, \Omega' \pm 1} [J(J+1) - \Omega'(\Omega' \pm 1)]^{1/2} \\ &\quad \times [j(j+1) - \Omega'(\Omega' \pm 1)]^{1/2}. \end{aligned} \quad (9)$$

Introduction of Eq. (6) into Eq. (5) provides, after diagonalization, the coefficients $b_{n''_b j \Omega}^{(i)}$ and the eigenvalues $E_{n''_b}^{(i)}$. Expansion (3) is then used to calculate the matrix elements of the total Hamiltonian (2). A final diagonalization provides the coefficients $a_{v'' n''_b n''_g}^{(i)}$ of Eq. (3) and the energies of the van der Waals bound states in the initial ground electronic state.

For the final continuum state, we expand the wave functions Ψ_{fE} as follows:

$$\Psi_{fE}(\mathbf{r}, \mathbf{R}) = \sum_{v, j, \Omega} \phi_{v, j, \Omega}^{(f, E)}(R) \times \chi_v^{(f)}(r) \Theta_{j \Omega}^{(J, M, p')}(\hat{r}, \hat{R}) \quad (10)$$

with the condition of appropriate asymptotic ($R \rightarrow \infty$) behavior, i.e.,⁹

$$\begin{aligned} \Psi_{fE} &\sim \chi_v^{(f)}(r) \Theta_{j \Omega}^{(J, M, p')}(\hat{r}, \hat{R}) e^{ik_{vj}R} \\ &\quad + \sum_{v', j', \Omega'} S_{vj \Omega, v' j' \Omega'}^* \chi_{v'}^{(f)}(r) \Theta_{j' \Omega'}^{(J, M, p')}(\hat{r}, \hat{R}) \\ &\quad \times e^{-ik_{v' j'} R}, \end{aligned} \quad (11)$$

where $k_{vj} = \sqrt{2m(E - E_v^{(f)} - B_v^{(f)} j(j+1))}$. Introduction of expansion (10) into the time independent Schrödinger equation leads to the close coupled system

$$\begin{aligned} &\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2mR^2} [J'(J'+1) + j(j+1) - 2\Omega^2] + E_v^{(f)} \right. \\ &\quad \left. + B_v^{(f)} j(j+1) + \langle \Theta_{j \Omega}^{(J, M, p')} | W_{vv}^{(f)} | \Theta_{j \Omega}^{(J, M, p')} \rangle - E \right\} \phi_{v, j, \Omega}^{(f, E)}(R) \\ &= - \sum_{v' j' \neq v j} \langle \Theta_{j \Omega}^{(J, M, p')} | W_{vv'}^{(f)} | \Theta_{j' \Omega'}^{(J, M, p')} \rangle \phi_{v', j', \Omega'}^{(f, E)}(R) - \frac{1}{2mR^2} \sum_{\Omega' \neq \Omega} \langle \Theta_{j \Omega}^{(J, M, p')} | l^2 | \Theta_{j \Omega'}^{(J, M, p')} \rangle \phi_{v, j, \Omega'}^{(f, E)}(R) \end{aligned} \quad (12)$$

From a given initial ground state $|\Psi_i\rangle$ and for a given transition $J''p'' \rightarrow J'p'$ the partial photodissociation cross section at energy E to produce diatomic fragments in the vibrational state v and the rotational state j will be given by³ (see also the Appendix):

$$\sigma_{f_{vj}E-i} \propto \sum_{\Omega} \left| \sum_{v'j'\Omega'} \sum_{v''j''\Omega''} (2j' + 1)^{1/2} (2j'' + 1)^{1/2} \right. \\ \times (1 + |\delta_{\Omega'0} - \delta_{\Omega''0}|)^{1/2} \\ \times \begin{pmatrix} J' & 1 & J'' \\ -\Omega' & t & \Omega'' \end{pmatrix} \begin{pmatrix} j' & 1 & j'' \\ -\Omega' & t & \Omega'' \end{pmatrix} \begin{pmatrix} j' & 1 & j'' \\ 0 & 0 & 0 \end{pmatrix} \\ \left. \times \langle \phi_{v'j'\Omega'}^{(f_{vj}\Omega E)} | \phi_{v''j''\Omega''}^{(i)} \rangle_R \langle \chi_{v'}^{(f)} | \mu_0(r) | \chi_{v''}^{(i)} \rangle_r \right|^2, \quad (13)$$

where we have defined

$$\phi_{v''j''\Omega''}^{(i)}(R) = \sum_{n''_a n''_b} a_{v''n''_a}^{(i)} b_{n''_b j''\Omega''}^{(i)} \chi_{n''_a}^{(i)}(R). \quad (14)$$

Equation (13) constitutes our final expression for the full 3D calculation of partial photofragmentation cross sections. We have assumed that the transition dipole moment μ_0 is not affected by complexation and therefore it depends only on r . The total cross section

$$\sigma_{fE-i} = \sum_{vj} \sigma_{f_{vj}E-i} \quad (15)$$

provides as a function of E the photofragmentation line shape. Finally, the rotational and vibrational distribution of the fragments is given by

$$P_{vj} = \frac{\sigma_{f_{vj}E-i}}{\sigma_{fE-i}}. \quad (16)$$

B. Vibrational diabatic decoupling and the golden rule approximation

In weakly coupled complexes like Ne...ICl, there is a natural decoupling between the “fast” vibrational motion of ICl and the intermolecular “slow” vibrations.¹² Therefore a very good zero-order approximation for the wave functions Ψ can be obtained by restricting the sum over v in Eqs. (3) and (10) to only one vibrational state of the diatomic

$$\Psi_v(\mathbf{r}, \mathbf{R}) = \chi_v(r) \Phi_v(R, \hat{\mathbf{r}}, \hat{\mathbf{R}}) \quad (17)$$

with Φ_v being the eigenfunction of the zero-order Hamiltonian

$$H_v = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \frac{I^2}{2mR^2} + B_v \frac{j^2}{\hbar^2} + E_v \\ + W_{vv}(R, \theta). \quad (18)$$

Equations (17) and (18) constitute the vibrational diabatic approximation. Since $W_{vv}(R, \theta)$ is an attractive potential, the channel Hamiltonians will have discrete as well as continuum eigenvalues. They will be coupled by the off-diagonal matrix elements $W_{vv'}(R, \theta)$ of the intermolecular potential. Since the coupling is weak, in most cases the problem can be described in a very good approximation by an isolated zero-order discrete level corresponding to the quasibound state Ne...ICl(B, v')

$$\Psi_{f_{v'}}(\mathbf{r}, \mathbf{R}) = \chi_{v'}^{(f)}(r) \Phi_{f_{v'}}(R, \hat{\mathbf{r}}, \hat{\mathbf{R}}) \quad (19)$$

coupled to a set of final zero-order continua

$$\Psi_{f_{vj}\Omega E}(\mathbf{r}, \mathbf{R}) = \chi_v^{(f)}(r) \Phi_{f_{vj}\Omega E}(R, \hat{\mathbf{r}}, \hat{\mathbf{R}}) \quad (20)$$

with $v < v'$, corresponding asymptotically to Ne + ICl(B, v, j). The Franck–Condon factors will strongly favour the optical transition between the initial ground state $|\Psi_i\rangle$ and the excited discrete state $|\Psi_{f_{v'}}\rangle$, whereas direct optical excitation of the continuum states will be extremely weak. We are thus in the situation of vibrational predissociation with pure Lorentzian line shape. Under these conditions, the partial photodissociation cross section will be given by¹²

$$\sigma_{f_{vj}E-i} \propto \sum_{\Omega} \frac{|\langle \Phi_{f_{vj}\Omega E} | W_{vv'}^{(f)} | \Phi_{f_{v'}} \rangle|^2}{(E - E_{f_{v'}})^2 + \Gamma_{f_{v'}}^2} \\ \times |\langle \Psi_{f_{v'}} | \boldsymbol{\mu} \cdot \mathbf{e} | \Psi_i \rangle|^2 \quad (21)$$

with

$$\Gamma_{f_{v'}} = \pi \sum_{vj\Omega} |\langle \Phi_{f_{vj}\Omega E} | W_{vv'}^{(f)} | \Phi_{f_{v'}} \rangle|^2 \quad (22)$$

being the half-width at half-maximum (HWHM) of the resonance. The associated lifetime for vibrational predissociation will be given by: $\tau_{f_{v'}} = \hbar/2\Gamma_{f_{v'}}$. The total cross section is

$$\sigma_{fE-i} = \sum_{vj} \sigma_{f_{vj}E-i} \\ \propto \frac{\Gamma_{f_{v'}}}{(E - E_{f_{v'}})^2 + \Gamma_{f_{v'}}^2} |\langle \Psi_{f_{v'}} | \boldsymbol{\mu} \cdot \mathbf{e} | \Psi_i \rangle|^2 \quad (23)$$

and the final state distribution will be

$$P_{vj} = \frac{\sigma_{f_{vj}E-i}}{\sigma_{fE-i}} = \frac{\pi}{\Gamma_{f_{v'}}} \sum_{\Omega} |\langle \Phi_{f_{vj}\Omega E} | W_{vv'}^{(f)} | \Phi_{f_{v'}} \rangle|^2 \\ \text{with } E = E_{f_{v'}}, \quad (24)$$

where we assume that the matrix elements $\langle \Phi_{f_{vj}\Omega E} | W_{vv'}^{(f)} | \Phi_{f_{v'}} \rangle$ are smooth functions of E in the region $E = E_{f_{v'}} + \Gamma_{f_{v'}}$. We need now to specify further the wave functions $\Phi_{f_{v'}}$ and $\Phi_{f_{vj}\Omega E}$. The discrete wave function $\Phi_{f_{v'}}$ is calculated using the same procedure as for the ground discrete state [see Eqs. (3) to (9)] for the particular vibrational channel v' of the B state. Thus

$$\Phi_{f_{v'}} = \sum_{n'_a n'_b} a_{n'_a n'_b}^{(f_{v'})} \chi_{n'_a}^{(f)}(R) \chi_{n'_b}^{(f)}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) \quad (25)$$

with

$$\chi_{n'_b}^{(f)}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = \sum_{j'\Omega'} b_{n'_b j'\Omega'}^{(f)} \Theta_{j'\Omega'}^{(J'M'p')}(\hat{\mathbf{r}}, \hat{\mathbf{R}}). \quad (26)$$

Similarly for the continuum wave functions we shall write

$$\Phi_{f_{vj}\Omega E} = \sum_{j'\Omega'} \phi_{f_{vj}\Omega E}^{(f_{vj}\Omega E)}(R) \Theta_{j'\Omega'}^{(J'M'p')}(\hat{\mathbf{r}}, \hat{\mathbf{R}}), \quad (27)$$

$\phi_{f_{vj}\Omega E}^{(f_{vj}\Omega E)}$ being the solutions of the coupled equations (12) for a single v .

Using Eqs. (25) to (27) together with Eqs. (7) and (8), the matrix elements $\langle \Phi_{f_{vj}\Omega E} | W_{vv'}^{(f)} | \Phi_{f_{v'}} \rangle$ appearing in the final expressions (21) to (24) can be written

$$\begin{aligned} \langle \Phi_{f\nu\Omega E} | W_{vv'}^{(f)} | \Phi_{f\nu'} \rangle &= \sum_{\Omega'} \int_0^\pi \sin \theta d\theta \int_0^\infty dR \\ &\times \varphi_{\Omega'}^{(f\nu\Omega E)*}(R, \theta) W_{vv'}^{(f)}(R, \theta) \\ &\times \varphi_{\Omega'}^{(f\nu')}(R, \theta), \end{aligned} \quad (28)$$

where we have defined

$$\varphi_{\Omega'}^{(f\nu')}(R, \theta) = \sqrt{2\pi} \sum_f \phi_{f\Omega'}^{(f\nu')}(R) Y_{f\Omega'}(\theta, 0), \quad (29)$$

with

$$\phi_{f\Omega'}^{(f\nu')}(R) = \sum_{n'_i, n'_b} a_{n'_i, n'_b}^{(f\nu')} b_{n'_i, n'_b}^{(f)} \chi_{n'_i}^{(f)}(R) \quad (30)$$

and

$$\varphi_{\Omega'}^{(f\nu\Omega E)}(R, \theta) = \sqrt{2\pi} \sum_f \phi_{f\Omega'}^{(f\nu\Omega E)}(R) Y_{f\Omega'}(\theta, 0). \quad (31)$$

In this treatment the coupling between the stretching (R) and rotational (θ) motions is treated explicitly. Therefore this is an exact 2D calculation. We shall refer to it as the diabatic vibrational golden rule (DVGR) treatment. The approximations used in establishing Eqs. (21) to (24) are the following:

- (1) A diabatic zero-order separation of the intramolecular vibrational motion, i.e., the internuclear distance (r) of ICl.
- (2) the assumption of an isolated resonance ($\Gamma \ll \Delta E_{\text{vdw}}$).
- (3) the assumption of smooth the discrete-continuum matrix elements as a function of energy ($\Delta V/V \ll 1$ for $\Delta E \sim \Gamma$).

C. Rotational infinite order sudden approximation (RIOSA)

Since in the final dissociative channels, the motion along the stretching coordinate (R) is presumably faster than the rotation of ICl (θ coordinate), the rotational infinite order sudden approximation (RIOSA)^{13,14} should be applicable. We shall then write

$$\varphi_{\Omega'}^{(f\nu\Omega E)} = \sqrt{2\pi} \delta_{\Omega\Omega'} \phi_{j_0\Omega}^{(f\nu E)}(R; \theta) Y_{j_0\Omega}(\theta, 0), \quad (32)$$

where $\phi_{j_0\Omega}^{(f\nu E)}(R; \theta)$ is the solution at energy E of H_v , Eq. (18) for a fixed value of the angle θ :

$$\begin{aligned} &\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2mR^2} [J(J+1) + j_0(j_0+1) - 2\Omega^2] \right. \\ &\quad \left. + E_v^{(f)} + B_v^{(f)} j_0(j_0+1) + W_{vv}^{(f)}(R, \theta) - E \right\} \\ &\times \phi_{j_0\Omega}^{(f\nu E)}(R; \theta) = 0, \end{aligned} \quad (33)$$

with j_0 being some averaged final rotational quantum number (usually taken as zero). Notice that Ω is also considered to be decoupled. Thus the coupled equations (12) are reduced to a one-dimensional Schrödinger equation which is solved for several values of θ . On the other hand, the quasi-bound wave function $\Phi_{f\nu'}$ is calculated without using the RIOSA. The matrix elements (28) are then given by

$$\begin{aligned} \langle \Phi_{f\nu\Omega E} | W_{vv'}^{(f)} | \Phi_{f\nu'} \rangle &= \sqrt{2\pi} \int_0^\pi \sin \theta d\theta \int_0^\infty dR \\ &\times (\phi_{j_0\Omega}^{(f\nu E)}(R; \theta) Y_{j_0\Omega}(\theta, 0))^* \\ &\times W_{vv'}^{(f)}(R, \theta) \varphi_{\Omega'}^{(f\nu')}(R, \theta) \end{aligned} \quad (34)$$

with $\varphi_{\Omega'}^{(f\nu')}(R, \theta)$ defined by Eq. (29).

III. MODEL POTENTIAL FOR THE Ne...ICl SYSTEM

The intermolecular potential energy surface used in this work to describe the Ne...ICl system was written as a sum of atom-atom pairwise interactions

$$W(r, R, \theta) = V_{\text{NeI}}(R_{\text{NeI}}) + V_{\text{NeCl}}(R_{\text{NeCl}}), \quad (35)$$

where the distances R_{NeI} and R_{NeCl} between pair of atoms are related to r , R and θ by

$$\begin{aligned} R_{\text{NeI}} &= [R^2 + (\gamma r)^2 - 2\gamma Rr \cos \theta]^{1/2}, \\ R_{\text{NeCl}} &= [R^2 + (1 - \gamma)^2 r^2 + 2(1 - \gamma)Rr \cos \theta]^{1/2} \end{aligned} \quad (36)$$

with $\gamma = m_{\text{Cl}}/(m_{\text{Cl}} + m_{\text{I}})$. The following masses were used in the calculations: $m_{\text{Ne}} = 20.18$ amu, $m_{\text{I}} = 126.9$ amu, and $m_{\text{Cl}} = 34.97$ amu.

All the individual interactions $V_{\text{AB}}(R_{\text{AB}})$ in Eq. (35) are described by Morse functions:

$$\begin{aligned} V_{\text{AB}}(R_{\text{AB}}) &= D_{\text{AB}} \{ \exp[-2\alpha_{\text{AB}}(R_{\text{AB}} - \tilde{R}_{\text{AB}})] \\ &\quad - 2 \exp[-\alpha_{\text{AB}}(R_{\text{AB}} - \tilde{R}_{\text{AB}})] \}. \end{aligned} \quad (37)$$

The parameters D_{AB} , α_{AB} , and $\tilde{R}_{\text{AB}}$ for the interatomic van der Waals interactions V_{NeI} and V_{NeCl} have been obtained by a multiproperty fitting of the available experimental data (dissociation energy, order of magnitude of the lifetime, and final rotational distribution) using the RIOSA¹⁴ approximation. Since the experimental spectra show no van der Waals progressions, we have taken for simplicity the same intermolecular parameters for the ground and excited electronic states.

A Morse function was also used for the intramolecular potential V_{ICl} . The parameters D_{ICl} , α_{ICl} , and $\tilde{R}_{\text{ICl}}$ were obtained from Ref. 15 using the relationships

$$\begin{aligned} \tilde{R}_{\text{ICl}} &= r_e; \quad \alpha = (2\mu\omega_e\chi_e/\hbar)^{1/2}, \\ D &= \hbar\omega_e/4\chi_e. \end{aligned} \quad (38)$$

All the potential parameters used in the calculations are given in Table I. As for the rotational constant of ICl($B, v=2$), we have used the value $8.154\,925 \times 10^{-2}$ cm⁻¹. In Fig. 1 we present a contour plot of the intermolecular potential for ICl being held fixed at its equilibrium distance. The minimum of the potential with respect to the lowest dissociation threshold is $D_e = -60.7$ cm⁻¹ at $R_e = 4.95$ Å and $\theta_e = 140^\circ$. Recently, Janda *et al.*¹ suggested that a different interpretation of the experimental final state rotational distribution for vibrational predissociation of Ne...ICl($A, v'=23$), may lead to larger values for the bond energy of the complex in the ground state. If this is the case, then the bond energy for the B state should also be modified.

TABLE I. Potential parameters for the Ne...ICl(*B*) potential energy surface.

	<i>D</i> (cm ⁻¹)	<i>α</i> (Å ⁻¹)	<i>R̄</i> (Å)
ICl	1270.4	3.96	2.66
NeI	26.0	1.80	5.40
NeCl	34.7	1.90	3.61

IV. RESULTS OF THE CALCULATIONS AND DISCUSSION

We have conducted full 3D photofragmentation cross section calculations for Ne...ICl in the spectral region corresponding to the transition $B \leftarrow X$. As expected, when the energy of the photon is varied, narrow lines are found in the near vicinity of the quasibound van der Waals levels. They are broadened by vibrational predissociation according to the reaction scheme

The v , n_s , and n_b labels are used to identify the van der Waals levels. For the lower states, the quantum numbers v (associated to the vibrational basis set of the ICl molecule), n_b and n_s (associated, respectively, to the bending and the stretching basis sets), are fairly good quantum numbers (coefficients of the expansion squared larger than 90%). Therefore the lowest van der Waals level for a given vibrational state v of the ICl molecule, corresponds mainly to a $n_b = 0$, $n_s = 0$ configuration. We have studied in detail the resonance associated with the level $B(v' = 2, n_s' = 0, n_b' = 0)$ for which experimental results are available. In order to gain some insight into the dynamics of this system we have also studied the resonance $B(v' = 2, n_s' = 0, n_b' = 1)$, which corresponds to excitation of the bending mode, and the $B(v' = 1, n_s' = 0, n_b' = 0)$ associated to a lower vibrational state of the ICl molecule.

All the calculations were conducted for zero total angular momentum ($J = 0$) in the excited state, and we have considered the transition from the rotational level $J'' = 1$, $\Omega'' = 1, p'' = -1$ of the ground electronic state. Therefore, the cross sections have been computed using [see Eq. (13)]

$$\sigma_{fijE-i} \propto \left| \sum_{v'j'} \sum_{v''j''} (2j' + 1)^{1/2} (2j'' + 1)^{1/2} \right. \\ \times \begin{pmatrix} j' & 1 & j'' \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} j' & 1 & j'' \\ 0 & 0 & 0 \end{pmatrix} \\ \left. \times \langle \phi_{v'j'0}^{(fij0E)} | \phi_{v''j''1}^{(i)} \rangle_R \langle \chi_{v''}^{(j)} | \mu_0(r) | \chi_{v'}^{(j)} \rangle_r \right|^2. \quad (40)$$

The calculation of the final dissociative wave functions was conducted with 5 vibrational channels ($v' = 0 - 4$) and about 40 rotational channels for each vibrational state (actually, 50 for $v' = 0$, 40 for $v' = 1 - 3$ and 30 for $v' = 4$). Therefore the full calculation implied 200 coupled equations. Below we present the convergence study. For the ini-

tial bound and quasibound states we used 30 bending and 15 stretching states in our basis set. Under these conditions, the accuracy is better than 10^{-3} cm⁻¹ for the energies of the lowest levels, 10^{-5} cm⁻¹ for the linewidths, and 0.01% for the final state distributions.

A. Full 3D calculation of the $B(v' = 2, n_s' = 0, n_b' = 0)$ resonance

In Fig. 2 we present, as a function of energy, the calculated total cross section for photofragmentation of Ne...ICl in the region of the $B(v' = 2, n_s' = 0, n_b' = 0)$ resonance. We obtain a pure Lorentzian line shape with total width $2\Gamma = 2.12 \times 10^{-3}$ cm⁻¹. This corresponds to a lifetime for vibrational predissociation of $\tau = \hbar/2\Gamma = 2.5$ ns. The resonance is centered at $E = -42.3647$ cm⁻¹ below the dissociation threshold for ICl($B, v' = 2$) production. Since the minimum of the potential energy surface $W_{v'v''}(R, \theta)$ for $v' = 2$ is at ~ 60 cm⁻¹ from the threshold, we conclude that the zero-point energy of the van der Waals modes is ~ 18 cm⁻¹.

Using Eq. (16) we have calculated the rotational distribution of the ICl($B, v = 1$) fragments. The results are presented in Table II where we compare several 3D calculations with different number of final vibrational channels. It is seen that good convergence is obtained with five vibrational channels ($v = 0$ to 4). Notice that in this case the sum of the probabilities is slightly different from 1 since there is $\sim 1\%$ probability for dissociation into the Ne + ICl ($v = 0$) channel (the $\Delta v = -2$ channel). The converged rotational dis-

FIG. 2. Photofragmentation cross section in the energy region of the Ne...ICl($B, v' = 2, n_s' = 0, n_b' = 0$) resonance. The zero of energy corresponds to -42.3647 cm⁻¹ below the Ne-ICl($B, v' = 2$) dissociation threshold. The points are the full 3D results. The solid line is a Lorentzian fit from which the full width ($2\Gamma = 2.12 \times 10^{-3}$ cm⁻¹) has been extracted.

TABLE II. Final state rotational distributions in the Ne + ICl ($v = 1$) dissociative channel following predissociation of the Ne...ICl ($v' = 2, n'_i = 0, n'_o = 0$) level.

j	3D ($v = 1-2$)	3D ($v = 1-3$)	3D ($v = 0-3$)	3D ($v = 0-4$)	DVGR
0	0.6903	0.5469	0.4943	0.4894	0.4956
1	1.1067	0.8629	0.7681	0.7600	0.7640
2	0.3450	0.2508	0.2066	0.2036	0.1914
3	0.1470	0.1371	0.1270	0.1264	0.1091
4	1.0442	0.9007	0.8323	0.8266	0.8146
5	1.6171	1.3359	1.1908	1.1804	1.1644
6	1.0624	0.8611	0.7289	0.7220	0.6805
7	0.6000	0.5908	0.5290	0.5290	0.4403
8	1.5623	1.5701	1.5055	1.5059	1.3699
9	3.0586	2.9093	2.7539	2.7489	2.5933
10	3.2781	3.1280	2.9306	2.9263	2.7833
11	2.8266	2.9101	2.7827	2.7872	2.6779
12	3.8612	4.0837	4.0299	4.0393	3.9655
13	5.9615	6.1216	6.0638	6.0711	5.9904
14	6.7131	6.8907	6.8256	6.8337	6.7044
15	6.1760	6.5124	6.5091	6.5226	6.3982
16	6.4874	6.8659	6.9419	6.9564	6.9503
17	7.6260	7.8945	8.0028	8.0128	8.1535
18	7.7296	7.9410	8.0526	8.0600	8.2620
19	6.7021	6.9165	7.0375	7.0444	7.2304
20	5.9698	6.1025	6.2314	6.2348	6.4117
21	5.7151	5.7133	5.8333	5.8316	6.0204
22	5.0487	4.9867	5.0875	5.0836	5.2596
23	3.9237	3.8592	3.9401	3.9362	4.0684
24	2.9992	2.9100	2.9715	2.9669	3.0528
25	2.4032	2.2830	2.3266	2.3211	2.3754
26	1.8308	1.7172	1.7468	1.7418	1.7858
27	1.2581	1.1710	1.1901	1.1863	1.2325
28	0.8459	0.7751	0.7864	0.7833	0.8197
29	0.5820	0.5231	0.5293	0.5269	0.5398
30	0.3700	0.3292	0.3327	0.3311	0.3213
31	0.2061	0.1821	0.1839	0.1830	0.1709
32	0.1146	0.9977 - 1	0.1004	0.9985 - 1	0.9679 - 1
33	0.6891 - 1	0.5926 - 1	0.5946 - 1	0.5908 - 1	0.5676 - 1
34	0.3986 - 1	0.3410 - 1	0.3420 - 1	0.3397 - 1	0.2852 - 1
35	0.1910 - 1	0.1620 - 1	0.1624 - 1	0.1613 - 1	0.1291 - 1
36	0.8205 - 2	0.6869 - 2	0.06866 - 2	0.6815 - 2	0.6334 - 2
37	0.1529 - 2	0.1251 - 2	0.1248 - 2	0.1239 - 2	0.1063 - 2
38	0.9768 - 8	0.7927 - 8	0.7925 - 8	0.7866 - 8	0.8151 - 8
39	0.2071 - 12	0.1590 - 12	0.1612 - 12	0.1600 - 12	0.1523 - 12

FIG. 3. Full 3D calculated rotational distribution (solid line) of ICl fragments resulting from vibrational predissociation of the ($v' = 2, n'_i = 0, n'_o = 0$) level of Ne...ICl(B). The dashed line are the experimental results of Ref. 6.

tribution has been plotted on Fig. 3, together with the experimental results of Lester and collaborators. The agreement between calculated and experimental results is good considering the very simple form of the potential used. Presumably a better agreement could be obtained by allowing some of the parameters to change but this has not been attempted in this work. In particular, it could be interesting to see the effect of changing the bond energy (which has been suggested¹ to be larger than the one used in this work) on the rotational distribution for the higher levels. In addition, the inclusion of the correct electrostatic (dipole-induced dipole) asymptotic behavior of the intermolecular potential may change somewhat the results. The study of this effect and the determination of a better set of potential parameters is left for future work.

The rotational distribution presented in Fig. 3 corresponds to the $\Delta v = -1$ vibrational predissociation channel.

TABLE III. Calculated energies, halfwidths and lifetimes for some vibrational predissociated levels of Ne...ICl(*B*). The numbers on the top are the full 3D results while those in parenthesis were obtained using the DVGR approximation.

	$v' = 1$ $n'_s = 0 \cdot n'_b = 0$	$v' = 2$ $n'_s = 0 \cdot n'_b = 0$	$v' = 2$ $n'_s = 0 \cdot n'_b = 1$
$E(\text{cm}^{-1})$	-42.5694 (-42.5762)	-42.3647 (-42.3613)	-34.8658 (-34.8464)
$\Gamma(\text{cm}^{-1})$	.285 - 3 (.275 - 3)	.106 - 2 (.103 - 2)	.851 - 3 (.826 - 3)
$\tau(\text{ns})$	9.31 (9.66)	2.50 (2.59)	3.11 (3.21)

This corresponds to what has been measured experimentally. Since our converged calculation includes the $\Delta v = -2$ channel we have computed the branching ratio $(\Delta v = -2)/(\Delta v = -1)$ and the final state rotational distribution for $\Delta v = -2$. The calculated branching ratio is 1.3×10^{-2} . The small value of this ratio is consistent with the propensity rule for vibrational predissociation.¹² As for the final state rotational probabilities we have found that the $\Delta v = -2$ and $\Delta v = -1$ channels have very similar distributions. This fact has already been noted in the experiments (and calculations) on Ne...Cl₂(*B*).¹ It is in contradiction with what is expected from a simple impulsive model for energy release into rotation which predicts that rotational excitation should scale with the square root of the available energy.

B. Validity of the diabatic vibrational golden rule (DVGR) approximation

We now turn to a comparison between the full 3D results and the ones obtained within the DVGR approximation. From Table II we see that DVGR reproduces very well the full 3D rotational distribution. This is also true for the total linewidth as well as for the resonance position (see Table III). It should be noticed however, that the DVGR calculation includes only two vibrational channels: the initial channel ($v' = 2$) and the final channel ($v = 1$). In order to check the DVGR approximation it is then important to compare with a close-coupled calculation which includes the same two channels and only these two channels (first column in Table II). When this is done it is found that the agreement is rather poor. The total linewidth, for example, is off by as much as 20%. This indicates that some of the assumptions underlying the DVGR approximation are not valid. Since the resonances are well isolated ($\Gamma \sim 10^{-3} \text{ cm}^{-1} \ll \omega_b \sim 8 \text{ cm}^{-1} < \omega_s \sim 24 \text{ cm}^{-1}$), the golden rule approximation should be valid. On the other hand, the continuum-continuum couplings between different vibrational channels, which are neglected in the vibrationally diabatic approximation, are strong in this case and cannot be neglected. We conclude that the agreement between the DVGR and the full 3D results could be fortuitous and due to a compensation effect between the contribution of different vibrational channels.

C. Study of the rotational infinite order sudden approximation (RIOSA)

In Fig. 4 we present a comparison between the final state rotational distributions obtained with the full 3D calculation and the RIOSA treatment. We notice that the overall behavior of the exact rotational distribution is well reproduced by RIOSA, in particular, the main peak at $j \sim 17$ and the undulations. On the other hand, for the highest populated rotational states, the two distributions differ significantly, the RIOSA giving larger probabilities. This is expected since in the RIOSA calculation the final translational continuum wave functions do not depend on the fragments rotational energy and in addition, all final rotational channels are open. Hence the distribution predicted by RIOSA gives significant probabilities to rotational states which, for energetic reasons, will not be populated at all in the exact calculation. Actually, the average rotational energy of the ICl fragments amounts to about 20% of the total available energy. It is surprising that under these conditions the RIOSA worked so well. Although unexpected, this is a very useful result. As the RIOSA calculation implies much less computational effort than the full 3D, it is possible to use RIOSA to obtain a first estimate of the potential parameters before starting more thorough calculations. This is what has been done in this work.

D. Decomposition of the initial quasibound wave function in terms of free rotor states

In order to get insight into the details of the fragmentation dynamics, it is useful to analyze the initial predissociated quasibound wave function (from the DVGR calculation) in terms of free rotor states. This amounts to considering that the final state rotational distribution of the ICl fragment is obtained by a sudden bond breaking with no torque acting during the dissociation. The probability for detecting ICl in the rotational state j is then given by the square of the expansion coefficient of the quasibound state $|\Phi_{fv}\rangle$ in terms of the free rotor wave functions integrated over R . From Eqs. (25) and (26) we get

FIG. 4. Comparison between the rotational distribution obtained with RIOSA (dotted line) and the full 3D calculation (solid line) for the vibrational predissociation of the ($v' = 2 \cdot n'_s = 0 \cdot n'_b = 0$) level of Ne...ICl(*B*).

$$P_j = \sum_{\Omega} \int_0^{\infty} dR \left| \sum_{n'_s n'_b} a_{n'_s n'_b}^{(f\nu')} b_{n'_b j \Omega}^{(f)} \chi_{n'_s}^{(f)}(R) \right|^2$$

$$= \sum_{\Omega} \sum_{n'_s} \left(\sum_{n'_b} a_{n'_s n'_b}^{(f\nu')} b_{n'_b j \Omega}^{(f)} \right)^2. \quad (41)$$

The results of this calculation is presented in Fig. (5) together with the full 3D rotational distribution. It is clear that the two distribution are very different. Another calculation in which the initial wave function $|\Phi_{f\nu'}\rangle$ is multiplied by the coupling $W_{uv'}$ inducing the predissociation, gives very similar results. Hence, as have been suggested before,⁶ the highly inverted rotational distribution found for this system is due to final state interactions (torques) as the fragments separate. Classically one would expect that trajectories that start with a skewed orientation on the Cl atom side of the complex will induce maximum angular momentum transfer (rainbow angle).¹⁶ Now, the equilibrium geometry of the Ne...ICl complex is at $\theta = 140^\circ$ and the initial wave function will have its maximum just in the region of the rainbow angle. Hence the highly inverted distribution.

It is interesting to compare these results with those obtained for the $X\cdots Cl_2$ ($X = He, Ne$).²⁻⁴ For the $X\cdots Cl_2$ systems the rotational distribution has a main peak for low j 's followed by a secondary maximum at high j 's. The interpretation of this result was the following:¹⁶ Since the $X\cdots Cl_2$ complexes are T shaped, most of the trajectories give no angular momentum transfer and therefore one expects a rotational distribution peaking at low j 's. However, the tail of the wave function of the initial quasibound state in the region of the rainbow angle gives rise to a secondary maximum at high j 's.

Another interesting feature of the calculations presented in Fig. 5 is the presence of pronounced oscillations with

FIG. 5. Comparison between the full 3D rotational distribution (solid line), obtained for the vibrational predissociation of Ne...ICl($B, v' = 2, n'_s = 0, n'_b = 0$) and the decomposition of the initial wave function in terms of free rotor states (dashed line).

maxima at $j = 1, 5, 9, \dots$ and minima at $j = 3, 7, 11, \dots$. They are the effect of the initial geometry of the complex. Oscillating rotational distributions of this type are well documented in the study of direct photodissociation of bent triatomic molecules.¹⁷ Since the initial wave function is approximately symmetric with respect the equilibrium angle, all the expansion coefficients of the free rotor wave functions which change sign in that region should vanish. As can be seen on Fig. 5, these oscillations are still present (although very much attenuated) in the full 3D results and the experiment (see Fig. 3) seems to confirm this finding. Therefore, oscillations in the final state rotational distribution could be important in determining the initial geometry of the complex.

E. Effect of excitation of the bending van der Waals mode

Although not detected experimentally due to very poor Franck-Condon factors in the excitation spectrum, the study of vibrational predissociation from excited van der Waals levels is important to understand the details of fragmentation dynamics in these systems. For the Ne...ICl complex the first excited van der Waals level corresponds mainly to one quantum of bending excitation ($n_s = 0, n_b = 1$) with very little mixing of other configurations. We have performed full 3D and DVGR calculations for the resonance Ne...ICl($B, v' = 2, n'_s = 0, n'_b = 1$). The results are presented in Table III and in Fig. 6, where we have also represented the projection of the quasibound wave function in terms of free rotor states.

As can be seen in Table III, the resonance position is 7.5 cm^{-1} above the ($n'_s = 0, n'_b = 0$) zero-point van der Waals level (which is consistent with a bending frequency of about 8 cm^{-1}), and its linewidth is about 50% narrower. This was also the case for the Ne...Cl₂ system.² This is consistent with the energy gap law.¹² Although going from one level to the next changes somewhat the initial wave function and therefore also the coupling matrix elements between the initial and final vibrational channels, the main effect is that an

FIG. 6. Same as Fig. 5 for the ($v' = 2, n'_s = 0, n'_b = 1$) level.

increase in energy makes the available translational energy greater and this increases the lifetime.

Since bending in the complex correlates with rotation in the products, one may expect that excitation of the bending mode will result in a substantial increase of the rotational excitation of the ICl fragment. From a comparison of Figs. 3 and 6, it is clear that this is not the case. Actually, the low j 's are more populated when the complex predissociates from the excited level than from the lowest state. The interpretation of this result is the following. For the lowest van der Waals level ($n'_s = 0$, $n'_b = 0$) the probability of finding the complex with a given angular configuration is maximum at $\theta = 140^\circ$ (the equilibrium geometry). As discussed above this should be very near the region of the rainbow angle or in other words, the angular configuration for which there is maximum angular momentum transfer. The excited bending wave function on the other hand, will have a node in that region. This will make the rotational excitation of the products smaller.

The fact that the wave function of the first excited van der Waals level has a node at 140° can also be seen in its initial rotational content as represented in Fig. 6. The state $j = 3$, which for the lowest van der Waals level has vanishing probability (see Fig. 5), corresponds for the excited level to a maximum. The reason for this is that $P_3(\cos \theta)$ as a node around 140° . Similarly, due to the properties of $P_5(\cos \theta)$, $j = 5$ which corresponds to a maximum in Fig. 5 is a minimum in Fig. 6.

F. The vibrational dependence of the fragmentation dynamics

In order to study the vibrational dependence of the fragmentation dynamics, we have performed calculations for the resonance $\text{Ne} \cdots \text{ICl}(B, v' = 1, n'_s = 0, n'_b = 0)$. The resonance position and its lifetime (linewidth) obtained by a full 3D and by the DVGR treatment are presented in Table III. It is seen that the resonance shifts by 0.2 cm^{-1} towards lower energies when going from $v' = 1$ to $v' = 2$, and that its width increases by a factor of about 4. This superlinear dependence for vibrational predissociation rates was also found for other systems,¹ and is the result of two contributions: the intramolecular contribution, depending only on the properties of the free ICl molecule, and the intermolecular contribution depending on the relative translational energy of the fragments. In the harmonic approximation, the intramolecular factor varies linearly with v and the intermolecular factor is constant, so one expects an overall linear dependence of the vibrational predissociation rate in this approximation.¹² However, when the effect of anharmonicity is considered, the available energy going from one initial vibrational state to the next diminishes, and according to the energy gap law,¹² the intermolecular factor contributes with an additional v dependence.

V. CONCLUSION

We have conducted three-dimensional quantum mechanical calculations for the vibrational predissociation of the $\text{Ne} \cdots \text{ICl}$ van der Waals complex, corresponding to exci-

tation of the $B(v' = 1, 2)$ states of the ICl molecule. For the $v' = 2$ level, which has been studied experimentally, we were able to reproduce the final state rotational distribution of the ICl fragment using a sum of pairwise atom-atom potentials. The proposed potential energy surface has a minimum 60.7 cm^{-1} deep in the $\theta = 140^\circ$ configuration (see Fig. 1).

It is interesting to compare this system with $\text{Ne} \cdots \text{Cl}_2$ for which a potential energy surface was also adjusted to fit the experiments. The dissociation energy and the frequencies of the van der Waals modes are similar for the two systems. On the other hand, the geometries are very different. While $\text{Ne} \cdots \text{Cl}_2$ is T shaped, $\text{Ne} \cdots \text{ICl}$ is bent. This results in very different final state rotational distributions of the fragments. For $\text{Ne} \cdots \text{Cl}_2$ the distribution is bimodal with a main peak at $j \sim 4$ and a secondary small maximum at $j \sim 22$. For $\text{Ne} \cdots \text{ICl}$ the distribution is highly inverted with a maximum at $j \sim 17$. This corresponds to the complex having its equilibrium geometry in the region of maximum angular momentum transfer (the rainbow angle) and in this respect the $\text{Ne} \cdots \text{ICl}$ complex is a rather unique example of this circumstance.

In addition to the main peak, we have found undulations in the rotational distribution of the ICl fragment which are also due to the bent equilibrium geometry of the complex. It is suggested that an experimental measurement of this oscillations may provide a direct way of determining the exact geometry of the complex.

We have studied the validity of the DVGR approximation. Although all the conditions for the application of the golden rule approximation are met, we have found that for this system the vibrational interchannel (continuum-continuum) coupling is important and cannot be neglected. Nevertheless, due to a compensation effect, the DVGR approximation gives very good results when compared with the full converged 3D calculation. It could be interesting to check whether this is true for other systems as well.

We have also studied the validity of the RIOSA as applied to the calculation of the final continuum states. We have shown that qualitative agreement between the RIOSA and the full 3D results is obtained in spite of the fact that a substantial amount of the total available energy goes into rotation of the ICl fragment. This result demonstrates that RIOSA can be used to obtain a first estimate of the potential parameters for these systems.

Finally, we have studied the effect of the initial energy content on the vibrational predissociation dynamics. As in the $\text{Ne} \cdots \text{Cl}_2$ case,² we have found that when the van der Waals bending mode is excited the lifetime is longer than for the zero-point van der Waals level, a result which can be rationalized in terms of the energy gap law.¹²

The results presented in this work provides a rather detailed description of the fragmentation dynamics in $\text{Ne} \cdots \text{ICl}$. They also constitute quantum mechanical benchmark data which can be useful to test other methods and approximations.

ACKNOWLEDGMENTS

We are grateful to M. Lester for very stimulating discussions and for providing us with experimental results prior to

publication. The calculations presented in this paper have been conducted on the Fujitsu VP200 supercomputer at CIRCE (Orsay). We thank the Director of the MPB Department of the CNRS for a grant of computer time.

APPENDIX

The radiation-matter interaction operator $\mu \cdot e$ can be written:

$$\mu \cdot e = \sum_s \mu_s e_s^*, \quad (\text{A1})$$

where $\mu_0 = \mu_z$ and $\mu_{\pm 1} = \mp (\mu_x \pm i\mu_y)/\sqrt{2}$ are the tensorial components of the transition dipole operator in the space fixed system. In our case, the transition dipole operator lies along the ICl nuclear axis (parallel transition). Therefore,

$$\begin{aligned} & \langle \Theta_{J'\Omega'}^{(J'M'p')} | \mu \cdot e | \Theta_{J''\Omega''}^{(J''M''p'')} \rangle \\ &= \sum_{st} e_s^* \mu_0(r) (-1)^{M'} \begin{pmatrix} J' & 1 & J'' \\ -M' & s & M'' \end{pmatrix} (2J' + 1)^{1/2} (2J'' + 1)^{1/2} \\ & \times (1 + |\delta_{\Omega'0} - \delta_{\Omega''0}|)^{1/2} (2J' + 1)^{1/2} (2J'' + 1)^{1/2} \begin{pmatrix} J' & 1 & J'' \\ -\Omega' & t & \Omega'' \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ -\Omega' & t & \Omega'' \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (\text{A4})$$

with the selection rule $p' \neq p''$. Using Eq. (A.4) in Eq. (1), together with Eqs. (3), (6), and (10), Eq. (13) is obtained.

¹For a review see, K. C. Janda and C. R. Bieler in *Atomic and Molecular Clusters*, edited by E. R. Bernstein. (Elsevier, Amsterdam, 1989).

²N. Halberstadt, J. A. Beswick, and K. C. Janda, *J. Chem. Phys.* **87**, 3966 (1987).

³J. I. Cline, B. P. Reid, D. D. Evard, N. Sivakumar, N. Halberstadt, and K. C. Janda, *J. Chem. Phys.* **89**, 3535 (1988).

⁴J. I. Cline, N. Sivakumar, D. D. Evard, C. R. Bieler, B. P. Reid, N. Halberstadt, S. R. Hair, and K. C. Janda, *J. Chem. Phys.* **90**, 2605 (1989).

⁵N. Halberstadt, O. Roncero, and J. A. Beswick, *Chem. Phys.* **129**, 83 (1989).

⁶(a) J. M. Skene, J. C. Drobits, and M. I. Lester, *J. Chem. Phys.* **85**, 2329 (1986); (b) J. M. Skene, Ph.D. thesis, University of Pennsylvania, 1988.

⁷R. L. Waterland, M. Lester, and N. Halberstadt, *J. Chem. Phys.* (in press).

$$\mu_s = D_{s0}^{1*}(\varphi_r, \theta_r, 0) \mu_0, \quad (\text{A2})$$

where $D_{s0}^{1*}(\varphi_r, \theta_r, 0)$ is a rotational Wigner function of the polar angles θ_r and φ_r , specifying the orientation of the ICl nuclear axis with respect to the space-fixed system of reference. In our calculations we have used a body-fixed system of reference where the orientation of the diatomic molecule is specified by the polar angles θ and φ with respect to the R axis. The Wigner rotational function $D_{s0}^{1*}(\varphi_r, \theta_r, 0)$ can be written in terms of the body-fixed angles θ , φ , θ_R , φ_R using the transformation

$$D_{s0}^{1*}(\varphi_r, \theta_r, 0) = \sum_t D_{st}^{1*}(\varphi_R, \theta_R, 0) D_{t0}^{1*}(\varphi, \theta, 0). \quad (\text{A3})$$

Assuming that the transition dipole component μ_0 only depends on the internuclear distance r of the ICl molecule and using the known integrals between Wigner functions,¹¹ one obtains:

⁸B. P. Reid, K. C. Janda, and N. Halberstadt, *J. Phys. Chem.* **92**, 587 (1988).

⁹N. Halberstadt, J. A. Beswick and J. M. Launay (to be published).

¹⁰J. M. Launay, *J. Phys. B* **9**, 1823 (1976).

¹¹R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).

¹²J. A. Beswick and Jortner, *Adv. Chem.* **47**, 363 (1981).

¹³(a) D. Secrest, *J. Chem. Phys.* **62**, 710 (1975); (b) L. W. Hunter, *J. Chem. Phys.* **62**, 2855 (1975); (c) L. Eno and G. G. Galint-Kurti, *J. Chem. Phys.* **71**, 1447 (1979).

¹⁴J. A. Beswick and G. Delgado-Barrio, *J. Chem. Phys.* **73**, (1980) 3653.

¹⁵K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

¹⁶(a) R. L. Waterland, J. M. Skene, and M. Lester, *J. Chem. Phys.* **89**, 7277 (1989); (b) N. Halberstadt, R. Schinke, and J. A. Beswick (to be published).

¹⁷(a) J. A. Beswick and W. M. Gelbart, *J. Phys. Chem.* **84**, 3148 (1980); (b) R. Schinke, V. Engel, and V. Staemmler, *J. Chem. Phys.* **83**, 4522 (1985).