Atomic and Molecular Processes with Short Intense Laser Pulses

Edited by
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SOME THEORETICAL ASPECTS OF INFRARED MOLECULAR LASERS PUMPED
BY ELECTRONIC-TO-VIBRATIONAL ENERGY TRANSFER

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ABSTRACT

Pulsed infrared lasers in which the pumping mechanism is electronic-to-vibrational energy transfer are well known today in many practical situations. However, this selective process is still submitted to many theoretical objections in order to reach a close confrontation with the experimental data. This work can be seen as a contribution more to this respect. The Na-N₂ system is one of the main examples chosen in this field. Its study has been carried out in the C_{2v} configuration within the close-coupling framework, describing the N₂ molecule as an anharmonic oscillator.

INTRODUCTION

Intermolecular energy transfer is one of the elementary processes more carefully studied in the nonadiabatic molecular collisions. Within the low-energy regime, where the kinetic energy associated with nuclear motion is less than ~20 eV /1/, a great amount of phenomena of this type is found in planetary atmospheres, interstellar space, magnetohydrodynamics systems, chemical reaction dynamic and gas lasers. Special attention is receiving the quenching of resonance radiation where electronic to vibrational and rotational (E-V-R) energy transfer occurs in the collision of electronically excited alkali atoms with different diatomic or polyatomic partners. The most sophisticated experimental techniques, at present, are being applied /2a/ in order to improve our understanding of this process. Unfortunately, this tendency is not closely followed at theoretical level /2b/ or at least with the same intensity. A lack of availability of accurate potential energy surfaces and reasonable interelectronic couplings prevents more refined dynamical calculations.

It is well known that E-V-R energy transfer leads to a population inversion among final states. This process is selective and pumps the molecular partner into specific energy states. Infrared lasers have been built in the last years /3/

based on the following reactions:

where X are halogen atoms, M represents a polyatomic, the symbols * and † denote electronical and vibrational excitation, respectively, and ΔE is the energy defect. Triatomic or larger polyatomic molecules show a more resonant behavior than in the diatomic cases. The choice of the X atoms, halogen or not, affects to the values of the quenching cross sections observed. The corresponding energy transfer mechanisms are expected to be very different /2b/.

In this work, we have proposed to investigate some theoretical aspects about the quenching alkali resonance radiation in E-V energy transfer collisions with diatomic molecules. The existence of chemical lasers or even experimental works is well known, but not many theoretical calculations are to be present in the literature and, therefore, to get new information about the intimate nature of this process, we have chose the Na-N₂ system. It is one of the prototype molecular systems in this context for which reasonable three-dimensional potential energy surfaces are available/4/. As far as we know, potential energy surfaces together with the relevant interelectronic couplings have only been reported for a fixed N₂ bond length /5/, neglecting then the diatomic vibration. Following the ideas of some authors /4,6-9,12 /, we have proposed elsewhere /10/ an interelectronic coupling based on a curve-crossing model in order to stress the role of the N₂-vibration in the quenching process. This model yielded a moderated inversion of the diatomic vibrational population after the collision when the molecular subunit was described as an harmonic oscillator /10/ at the perpendicular configuration. On the contrary, in this paper, the diatom is taken as an anharmonic oscillator and a stronger inversion population and greater efficiency is obtained as compared with the harmonic case.

COUPLED EQUATIONS AND RESULTS

The dynamic of the quenching

at low-energy regime may be described fairly well on the C_{2v} symmetry, which is energetically the most favourable /2b/ for this reaction, the rotational degree of freedom being ignored.

It has been estimated /2b/ that a small amount of $\sim 9\%$ of the energy transferred into internal motion of N₂ is going to the rotational degree of freedom.

In our calculations, we have taken the potential energy surfaces reported in ref. 4 which are expressed in terms of the internal coordinates of the molecular system: an angle and

two distances, one describing the relative motion of Na with respect to the center of mass of N_2 and the other one the diatomic vibrational motion. Unlike Ref.4, we have assumed the N_2 molecule as an anharmonic oscillator. The corresponding parameters were taken from Herzberg /11/.

When the total wave function is expanded in terms of a basis set of electronic wave functions, which depend parametrically on the nuclear positions, and the two-dimensional nuclear wave functions are also expanded in a basis of anharmonic oscillators, we get, after substitution into the corresponding Schrödinger equation, the usual set of coupled equations for the relative motion /1/

$$\left[\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E - \varepsilon_\sigma - U_{\alpha\sigma, \alpha'\sigma}(R) \right] \phi_{\alpha\sigma}(R) = \sum_{\substack{\alpha'=\alpha \\ v'=v}} U_{\alpha\sigma, \alpha'v'}(R) \phi_{\alpha'v'}(R) \quad (2)$$

In this expression, μ is the reduced mass for the Na- N_2 system, ε_σ are the eigenvalues for the anharmonic oscillator, E is the total energy, $U_{\alpha\sigma, \alpha'\sigma}(R)$ is an effective potential energy curve at each α -electronic state and $U_{\alpha\sigma, \alpha'v'}(R)$ represent the interelectronic and internuclear couplings. The interelectronic coupling is modelled by a gaussian function and only two electronic states (the ground and the first excited state) are taken into account /4/.

Concerning with the electronic coupling, it is well accepted, in the light of many studies carried out in the last ten years, that the energy transfer is determined by the location of the crossing between the electronic surfaces. This idea was recognized firstly by Bjerre and Nikitin /6/ and after by Bauer, Fisher and Gilmore /7/. In a second step, Mc Guire and Bellum /8/ treated this problem by close-coupling calculations, modelling also this coupling. In the same spirit, two recent works /9,10/ have accomplished some calculations with the same goal. We have reported a curve-crossing model elsewhere, using a gaussian-type function. Doing that, our aim was to collect the vibrational arguments given about the quenching mechanism. As previously, the off-diagonal elements of the equation (2) are expressed by

$$U_{\alpha v, \alpha' v'}(R) = B \langle \chi_\sigma(r) | e^{-\beta [R - R_c(r)]^2} | \chi_{\sigma'}(r) \rangle \quad (3)$$

where χ_σ are now, eigenfunctions of the N_2 anharmonic oscillator and B , β and $R_c(r)$ the three parameters of the gaussian function. $R_c(r)$ represents the crossing curve of the two electronic surfaces and this, at first approximation, can be fitted to a straight line around the equilibrium position of the diatomic oscillator. In this way, the important role of the vibration, that was already pointed out by different authors /4,12/, is explicitly included in our calculations.

In table I we present partial quenching probabilities averaged by a Boltzmann distribution of the temperature. This calculation was performed using the value $B = 0.001$ and $\beta = 8$. (atomic units), that were chosen after some tests to reproduce the main features of the experiment. Convergence was achieved with thirteen channels in the upper state and nine the lower one.

TABLE I. Quenching probabilities $P_{0 \rightarrow n}$, where $v=0$ and $v'=n$ stand for the entry and exit vibrational channels, at different temperatures.

T(K)	$P_{0 \rightarrow 0}$	$P_{0 \rightarrow 1}$	$P_{0 \rightarrow 2}$	$P_{0 \rightarrow 3}$	$P_{0 \rightarrow 4}$	$\sum_n P_{0 \rightarrow n}$
200	3.9(-3)	2.6(-2)	3.6(-2)	3.0(-2)	1.8(-3)	9.67(-2)
400	4.3(-3)	2.3(-2)	4.0(-2)	3.1(-2)	4.4(-4)	9.86(-2)
600	4.5(-3)	2.0(-2)	4.2(-2)	3.0(-2)	7.4(-4)	9.84(-2)
800	4.6(-3)	1.8(-2)	4.3(-2)	2.9(-2)	1.0(-3)	9.75(-2)
1000	4.7(-3)	1.7(-2)	4.4(-2)	2.9(-2)	1.2(-3)	9.64(-2)
1200	4.8(-3)	1.6(-2)	4.4(-2)	2.9(-2)	1.4(-3)	9.54(-2)

Only one channel in the initial state and eight in the final one are open in the range of energies studied. The inversion of the final vibrational population appearing in this table is mainly due to the excited closed channels. The existence of quasibound levels could be responsible of this highly resonant process. In fact, some preliminary calculation about the lifetimes of the levels supported by the $v=1$ vibrational channel of the excited electronic state gave values comprises in the range of 8-14 ps. The approximation applied was within the "Golden-Rule" framework and the exit channels with a major population were $v'=3,4$. This fact could explain the placing of peaks of our distributions. Moreover, the behavior of these probabilities with the temperature for the harmonic case /10/ is exactly the opposite to the Table I, where the inversion of the vibrational population increases lightly and the total inelastic quenching probabilities decrease very smoothly in the range 200-1200 K. Once more, the location of the crossing-points is very important in order to understand the mechanism of this process. The diatomic anharmonicity shifts the potential energy surfaces and changes the interelectronic coupling yielding distributions peaked at higher levels and a stability of them in a wider range of temperature.

The experimental results of Silver et al. /13/ and Reiland et al. /14/ are taken to be compared with our results at $T=1200$ K. We obtain a bit narrower distribution of final internal energies for N_2 and the peak shifted to smaller vibrational energies (one /13/ or two /14/ quanta) with respect to these experimental works. Also, as regards the efficiency of the quenching process, we calculate that $\sim 26\%$ of the available total energy is transferred to N_2 faced to the reported values there, $\sim 30-40\%$ /13/ or $\sim 50\%$ /14/. Due to the minor incidence of the rotational degrees of freedom, as was already mentioned, these discrepancies may be attributed mainly to the potential energy surfaces used here. In fact, the peaking of the final vibrational diatomic distribution, in this model, is strongly dependent on the crossing of both surfaces meanwhile the corresponding spreading and the percentage of energy transferred to the internal motions of N_2 can be monitored by varying the values of the β and B parameters, respectively.

In conclusion, we have presented here some theoretical results on infrared molecular lasers pumped by E-V energy transfer. We have taken an hipotetic laser system ($Na-N_2$) that has been studied from a methodological point of view. Many other

quencher molecules may be even much more favourable in this respect. For example, triatomic (CO_2 , N_2O , etc.) or organic molecules with double or triple bonds are known to be extremely good quenchers of alkali resonance radiation and the observed population inversion among vibrational levels of the molecules is very important for this goal. Despite of a detailed study of a simple system, like Na-N_2 , already presents many difficulties, it is an useful starting point to treat more complicated molecular laser systems based on this mechanism of pumping.

REFERENCES

- /1/ J.C. Tully, in "Dynamics of Molecular Collision", edited by W.H. Miller (Plenum, New York, 1976), part B, pag.217.
- /2/ a) I.V. Hertel, in "The Excited State in Chemical Physics", Adv. Chem. Phys., XLV (Part 2), edited by J.W. McGowan (Wiley, New York, 1981) pag. 341.
b) I.V. Hertel, in "The Dynamics of the Excited State", edited by K.P. Lawley (Wiley, New York, 1982) pag. 475.
- /3/ A.B. Petersen, C. Witting and S.R. Leone, Appl.Phys.Lett. 27 (1975) 305; J. App. Phys., 47 (1976) 1051.
- /4/ P. Habitz, Chem. Phys., 54 (1980) 131; P. Archirel and P. Habitz, Chem. Phys., 78 (1983) 213.
- /5/ M. Persico, in "Spectral Line Shapes", Vol. III, De Gruyter, Berlin, 1985.
- /6/ A. Bjerre and E.E. Nikitin, Chem. Phys.Lett., 6 (1967) 438.
- /7/ E. Bauer, E.R. Fisher and F.R. Gilmore, J. Chem. Phys., 51 (1969) 4173.
- /8/ P. Mc. Guire and J.C. Bellum, J. Chem. Phys., 71 (1979) 1975.
- /9/ D. Poppe, D. Papierowska-Kaminski and V. Bonacic-Koutecky, J.Chem.Phys., 86 (1987) 822.
- /10/ J.Campos-Martínez, S. Miret-Artés, P. Villareal and G. Delgado-Barrio, Chem. Phys. (submitted).
- /11/ G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand Reinhold Company, New York, 1979.
- /12/ P. Botchwina, W. Meyer, I.V. Hertel and W. Reiland, J.Chem. Phys., 75 (1981) 5438.
- /13/ J.A. Silver, N.C. Blais and G.H. Kwei, J. Chem. Phys., 71 (1979) 3412.
- /14/ W. Reiland, C.P. Shulz, M.V. Tittes and I.V. Hertel, Chem. Phys., Lett., 91 (1982) 329.

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