Quantum dynamics of quasiresonant vibration-rotation energy transfer in Li$_2$-Ne scattering

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This Rapid Communication reports fully quantum-mechanical calculations of inelastic-scattering cross sections for Li$_2^*$ (v_i, j_i) + Ne → Li$_2^*$ (v_f, j_f) + Ne with $40 \leq j_i \leq 100$. The calculations are performed within the coupled-states approximation. They reveal large cross sections for vibrational relaxation to remarkably narrow final-rotational-state distributions. The theoretical cross sections reproduce the $\Delta j = -4\Delta v$ correlation observed experimentally. Comparison of the quantum-mechanical results to classical trajectory calculations confirms the accuracy of the latter procedure.

Recent experiments by Pritchard and co-workers[1] have uncovered a new atom-diatomic molecule collision phenomenon. They observe that low-energy collisions between highly rotationally excited Li$_2^*$ molecules and Ne atoms yield efficient vibration-rotation energy transfer to a narrow distribution of final rotational states. The quasiresonant nature of this process and the size of the cross sections are enhanced at low collision energies. The striking feature of the vibration-rotation (V-R) transfer is the strong negative correlation observed between changes in vibrational and rotational quantum number.

In contrast, molecular rotation plays a much different role in vibrational relaxation of molecules with little rotational excitation.[2] Although it enhances vibrational relaxation at low collision energies, the enhancement is much smaller than for Li$_2^*$-Ne and does not exhibit the narrow j_f distributions. Furthermore, vibrationally inelastic cross sections generally increase with collision energy,[3] unlike the trend in Li$_2^*$-Ne. The primary exception occurs when strong attractive forces are present, for example, in the vibrational relaxation of molecular ions.[4] Under conditions of high internal excitation, extensive V-R energy transfer has been noted previously in quasiclassical trajectory studies[5] of Ar+H$_2$, He+H$_2$, Ar+HCl, and Ar+OH.

A recent classical trajectory study has shown that each collision of a Ne atom with Li$_2^*$ is composed of a number of "collisionettes" which occur when the molecular axis of Li$_2$ rotates past the incoming Ne atom.[6] The fast rotational motion enhances vibrational relaxation in two ways; it greatly increases the "effective" collision velocity, and it shifts the timing of the impulses applied to the vibrational motion by the incoming atom. Thus, the classical trajectories also show large V-R cross sections and a strong correlation between Δj and Δv. What is surprising is that the correlation $\Delta j/\Delta v$ remains equal to -4 over a wide range of j_i ($45 \leq j_i \leq 80$). It does not follow the correlation expected for resonant V-R transfer. For $j_i < 45$ the correlation shifts to -6, while it becomes -2 for $j_i > 80$; there is a preference for even-integer slopes. The appearance of such a "quantum" effect from a classical study is intriguing and is attributed to frequency locking by

Pritchard and co-workers.[6]

While the classical trajectory study has provided an interesting picture of the collision dynamics, the vibrational and rotational motions of Li$_2$ are manifestly quantum mechanical in nature. It is therefore important to have a quantal study of V-R energy transfer in Li$_2^*$-Ne against which to compare the classical results. Furthermore, a quantum-mechanical study should itself provide insight into the quasiresonant energy-transfer dynamics. At first glance a quantal study would seem a daunting prospect. For such a highly excited system, solution of the close-coupled scattering equations would require a prohibitively large basis of angular momentum states. The coupled-states approximation (CSA) decouples the orbital and rotational angular momenta and significantly alleviates this difficulty; however, the calculation would remain extremely time consuming. Fortunately, nature itself lends a hand. The physical observation of energy transfer to very specific final states translates computationally to the fact that only a relatively small number of rotational states in the vicinity of j_i and j_f are required to describe accurately the collision dynamics.

Solution of the coupled quantum-mechanical scattering equations is carried out under the j_z conserving coupled-states approximation of McGuire and Kouri.[7] In this approach the Schrödinger equation is transferred from space-fixed to body-fixed coordinates. This transformation introduces a kinematic coupling of angular momentum states having different m; the intermolecular potential itself has no intermultiplet couplings. These are eliminated in the CSA by replacing the orbital angular momentum by $L^2 = \hbar^2 l(l+1)$. In effect, this implies that the quantization axis for rotation remains aligned with the internuclear vector throughout the collision.

The CSA produces for each value of m a set of scattering equations coupled in v and j. These are solved using the R matrix propagator method of Light and co-workers.[8] Typically, a basis set of seven vibrational states each with fifteen rotational states yields converged results; at small j_i or high collision energy the rotational basis must be enlarged. The calculations employ the breathing

ellipsoid potential[9]

$$V(R, \theta, r) = V_1 \exp\left[\frac{-R + \alpha(r - r_e)[1 + aP_2(\cos\theta)]}{L(1 + [1 - \beta(1 - r/r_e)]aP_2(\cos\theta))} \right],$$ (1)

used by Pritchard and co-workers.[6] Usually, the intermolecular potential is expanded in Legendre polynomials of $\cos(\theta)$ and in a power series for r in order to facilitate calculation of potential matrix elements. If many terms in this expansion are kept to ensure accuracy, calculation of the matrix elements can become time consuming. Instead, an approach based on the spectral theorem for operators is adopted. Matrices for $r - r_e$ and $\cos^2(\theta)$ are written in the v,j basis.[10] Since these operators commute,

they can be simultaneously diagonalized. The potential matrix is obtained by applying Eq. (1) to the diagonal representations of $r - r_e$ and $[\cos^2(\theta)]^{1/2}$ and transforming the result back to the v,j basis. Note that the transformation matrix needs to be determined only once at the beginning of the calculation.

Cross sections averaged over initial m and summed over final m are found from

$$\sigma(v_f, j_f \leftarrow v_i, j_i) = (2j_i + 1)^{-1} \sum_{m = -\min(j_i, j_f)}^{\min(j_i, j_f)} \sigma(v_f, j_f, m \leftarrow v_i, j_i, m).$$ (2)

It is observed that the inelastic cross sections are generally largest for $m = 0$ and decrease smoothly as m approaches $\pm \min(j_i, j_f)$. As expected, the V-R mechanism is most effective when molecular rotation is in the plane of the incoming Ne atom. The smooth variation of $\sigma(v_f, j_f, m \leftarrow v_i, j_i, m)$ with m enables the sum in Eq. (2) to be approximated by evaluating cross sections for only a few m and interpolating the others. The individual m cross sections reproduce the experimentally observed narrow j_f distributions and correlation between Δj and Δv over a wide range of m; exceptions occur near the limiting values of m. That the quasiresonant energy transfer depends weakly on m suggests that the CSA provides an accurate description of the collision dynamics. In fact, the agreement between the results shown in Figs. 1-3 and the experimental measurements[1] bears this out.

Figure 1 shows theoretical j_f distributions for the vibrational relaxation ($\Delta v = -1$) of $A\ ^1\Sigma_u^+ \mathrm{Li}_2(v_i = 5, j_i)$ by collisions with Ne.[11] A number of features are noteworthy.

The peak cross sections increase as a function of j_i, reaching a maximum value of $\sigma = 15$ Å^2 for $j_i = 64$. This value is in excellent agreement with the classical trajectory study.[6] There is a corresponding decrease in the widths of the j_f distributions. Both trends reproduce the experimental results.[1] They reflect the rising importance of the V-R mechanism with increasing rotational excitation.

FIG. 2. Final-state distributions for the collisional relaxation of Li$_2^*$ by Ne for various initial rotational excitations. The arrows mark the final states most closely resonant to the incoming channel.
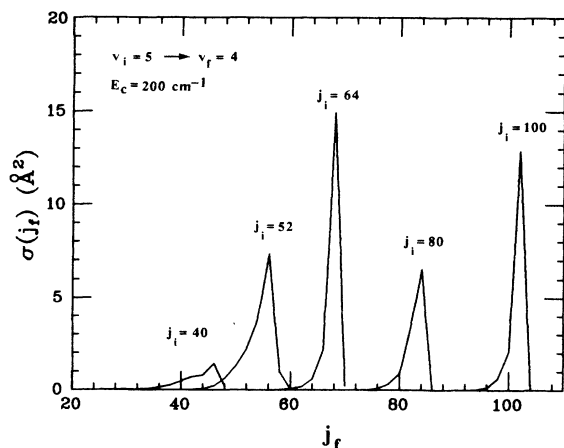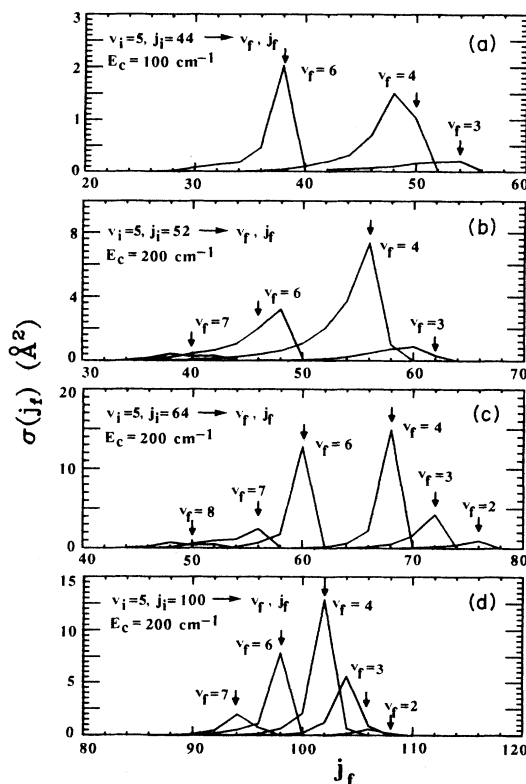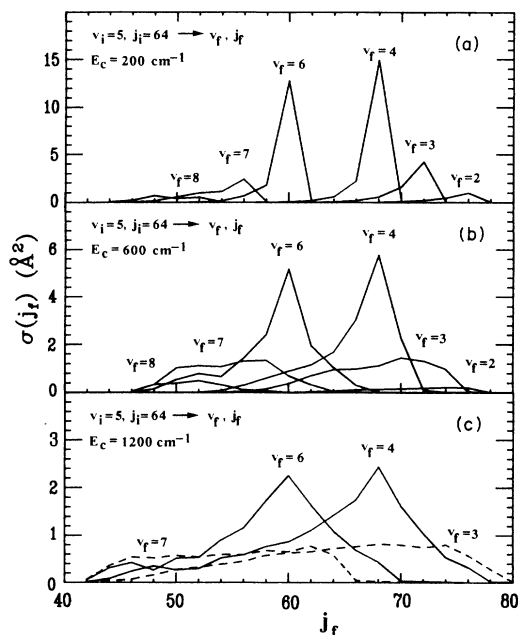

FIG. 1. Dependence of the $\Delta v = -1$ vibrational relaxation cross section and the width of the j_f distribution on initial rotational excitation.

FIG. 3. Dependence of the final-state distributions on collision energy for the inelastic scattering of Li_2^* ($v_i = 5$, $j_i = 64$) by Ne.

Most importantly, the CSA cross sections in Figs. 1 and 2 demonstrate the experimentally observed correlation between Δj and Δv. The correlation is $\Delta j/\Delta v = -4$ for $j_i = 52$, 64, and 80; however, it changes to $\Delta j/\Delta v = -2$ for $j_i = 100$ and to $\Delta j/\Delta v = -6$ for $j_i = 40$ and 44. These shifts are mirrored by the classical trajectory study. The present calculations show that when the initial rotational excitation lies in the regions over which the correlation changes slope, some vibrational transitions exhibit one correlation while other vibrational transitions will exhibit another. Figures 2(a), 2(b), and 2(d) provide examples of this.

The asymmetry of the j_f distributions evident in Figs. 1 and 2 is one of a number of features that is sensitive to the collision energy E_c. Figure 3 illustrates that the asymmetry decreases with increasing E_c. Larger collision energies also imply wider j_f distributions and smaller peak cross sections. For the example shown, the rotationally summed vibrationally inelastic cross sections also decrease. This is evidence that the quasiresonant V-R mechanism becomes progressively less important as the collision energy becomes greater.

We would like to understand the origin of a number of features in quasiresonant energy transfer. These include the correlation of Δj and Δv, the dependence of cross section on j_i and E_c, the dependence of j_f width on j_i and E_c, and the asymmetry of the j_f distributions. To do so, we examine the role of four factors in the collision dynamics: (1) energy mismatch between incoming and outgoing channel, (2) propensity of the potential coupling channels of various Δj and Δv, (3) proximity of threshold energy, and (4) collision energy.

Resonance is an important consideration in any quantum-mechanical system. Except for collision partners having strong attractive wells,[4] vibration-translation (V-T) relaxation is inefficient.[3] When the energy mismatch can be reduced, for example, by transfer of energy to rotation, vibrational relaxation becomes more efficient.[2] That energy mismatch plays an important role is evident in Fig. 2. A large number of vibrationally inelastic collisions result in population of the rotational state most nearly resonant with the incoming channel. In fact, at large j_i, cross section versus E_c for a given v_f approximately follows an exponential energy gap law; however, this deteriorates for small j_i. It is also clear, however, that resonance alone is not the determining factor in the V-R energy transfer. There are a number of exceptions; transitions that are not to the most resonant j_f instead preserve the $\Delta j = -4\Delta v$ correlation. The system apparently tries to preserve this correlation until it can no longer do so because the energy mismatch becomes too great.

The classical trajectory study suggests that frequency locking may be responsible for this behavior.[6] The quantum-mechanical view offers two other mechanisms. One is the propensity of the intermolecular potential to couple various asymptotic channels. Examination of the potential matrix reveals that off-diagonal elements become progressively smaller as Δj or Δv increase. Given a situation where two final rotational states have nearly equal energy mismatches, the tendency will be to populate the state with smaller Δj. The result is to preserve the $\Delta j = -4\Delta v$ correlation to smaller j_i, initial rotational states for which the rule $\Delta j = -6\Delta v$ would more closely satisfy resonance.

It has previously been shown that for vibrational relaxation of $\text{H}_2(v = 1, j = 0)$ by He enhancement by rotation is not due solely to reduction of the energy mismatch.[12] Rotation introduces a relative phase shift between incoming and outgoing wave functions that increases their overlap and hence the relaxation probability. The extent to which this mechanism is operative in the quasiresonant relaxation remains to be investigated.

At very low collision energies, it is possible that the final rotational state with smallest energy gap is energetically forbidden. For example, when E_c is lowered to 50 cm^{-1} the maxima in j_f for $j_i = 80$ in Fig. 1 and for $v_f = 6$ in Figs. 2(b) and 2(d) are not accessible; instead they shift to lower angular momentum by two units. The proximity of threshold energy also explains the asymmetry of the j_f distributions; they are truncated because energy conservation limits the extent of rotational excitation. Increasing the collision energy opens up more rotational states and reduces the asymmetry. An increase in E_c also yields wider j_f distributions. Two factors play a role in this. First, V-T relaxation becomes more likely and thus the energy mismatch is less important. Second, an increase in E_c permits closer approach of the Ne atom and thereby stronger coupling by the potential of the incoming channel to less energetically favorable final states.

In conclusion, it has been shown that it is possible to perform quantum-mechanical CS scattering calculations using a moderate size basis on a system with high internal excitation. The theoretical cross sections reproduce very well the recently discovered phenomenon[1] of quasiresonant V-R energy transfer in Li_2^*-Ne. For very low

collision energies and a purely repulsive intermolecular potential, efficient and state specific energy transfer is observed. The degree of resonance between incoming and outgoing channel is a key, but not the sole, factor in producing the very narrow final rotational distributions. The agreement between the classical study of Pritchard and co-workers[6] and the present quantal calculations with respect to features such as absolute cross sections, the widths of rotational distributions as a function of j_i and E_c, and the dependence of $\Delta j/\Delta v$ on j_i supports the accuracy of the classical study and the predictions made thereby.

[1]B. Stewart, P. D. Magill, T. P. Scott, J. Derouard, and D. E. Pritchard, Phys. Rev. Lett. **60**, 282 (1988).

[2]A. J. Banks, D. C. Clary, and H. J. Werner, J. Chem. Phys. **84**, 3788 (1986); A. J. Banks and D. C. Clary, *ibid.* **86**, 802 (1987); R. Schinke and G. H. F. Diercksen, *ibid.* **83**, 4516 (1985); D. R. Flower and D. J. Kirkpatrick, J. Phys. B **15**, 1701 (1982).

[3]J. T. Yardley, *Introduction to Molecular Energy Transfer* (Academic, New York, 1980); M. M. Maricq, E. A. Gregory, C. T. Wickham-Jones, D. J. Cartwright, and C. J. S. M. Simpson, Chem. Phys. **75**, 347 (1983); M. M. Maricq, E. A. Gregory, and C. J. S. M. Simpson, *ibid.* **95**, 43 (1985).

[4]E. E. Ferguson, J. Phys. Chem. **90**, 731 (1986); J. J. Tanner and M. M. Maricq, Chem. Phys. Lett. **138**, 495 (1987).

[5]N. C. Blais and D. G. Truhlar, J. Chem. Phys. **69**, 846 (1978); J. Phys. Chem. **86**, 638 (1982); D. L. Thompson, *ibid.* **86**, 630 (1982); *ibid.* **86**, 2538 (1982).

[6]P. D. Magill, B. Stewart, N. Smith, and D. E. Pritchard, Phys. Rev. Lett. **60**, 1943 (1988).

[7]P. McGuire and D. J. Kouri, J. Chem. Phys. **60**, 2488 (1974).

[8]E. B. Stechel, R. B. Walker, and J. C. Light, J. Chem. Phys. **69**, 3518 (1978).

[9]The constants employed in Ref. 6 are $V_1 = 759$ eV, $L = 0.381$ Å, $a = 0.325$, $\alpha = 0.566$, and $\beta = 0.5$.

[10]$\cos^2(\theta)$ is used because only even rotational states are coupled in a homonuclear molecule.

[11]Spectroscopic constants are obtained from K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, Princeton, 1979).

[12]J. J. Tanner and M. M. Maricq, Chem. Phys. **119**, 307 (1988).