Relaxation of highly vibrationally excited KBr by Ar

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Exact formulation of the impulse approach, also known as the quantum-mechanical spectator model, is used to investigate the rapid deactivation of highly internally excited KBr, written as KBr**, by Ar—a phenomenon not previously understood. The model of inelastic scattering at the repulsive wall, approximated here by a hard-core potential, using the impulse formalism is compared with the experimentally observed results obtained by scattering KBr** with Ar. The calculation is in excellent agreement with the measured results for the 75° center-of-mass (c.m.) scattering angle, while the calculated results for the 45° c.m. scattering near the peak (nearly elastic scattering) are a factor of about 1.5 smaller than the measured results. This is an impulse calculation where the collision energy is supplied by the internal motion of the target and not by the translational motion of the projectile.

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The past thirty years have seen a great deal of progress in the understanding of elementary collision processes [1]. The underlying mechanism for the relaxation of highly vibrationally and rotationally excited molecules, however, remains elusive. Fisk and co-workers [2–5], in a series of papers, have reported the relaxation of highly vibrationally excited KBr, denoted by KBr**, by various collision partners. KBr** produced by the reaction of K with Br_2 in a crossed molecular beam [6] has about 41 kcal/mole of vibrational energy (average vibrational quantum number ≈ 90) and is described by a rotational temperature of roughly 1500 K (average rotational quantum number ≈ 126). The KBr** beam thus produced is again crossed with another beam which may consist of Ar, N_2, CO, or other molecules at a modest collision energy of about 1 kcal/mole (roughly 0.04 eV). The relative differential cross section for the deactivation of KBr** as a function of the KBr recoil velocity for several scattering angles is measured for various collision partners. There are small differences in the shape of the curves for the relative differential cross section for different collision partners, but the important result of the experiments is that a substantial fraction of the roughly 2-eV internal energy may be converted into translational energy of relative motion in a single collision. This is not to imply that none of the internal energy of KBr** ends up as vibrational and rotational energy of its molecular collision partner. In fact, recoil velocities of KBr resulting from the collision of KBr** with CO_2 are smaller than those resulting from the collision with Ar. This may be the result of additional channels available resulting from the collision with CO_2. The conclusion is that the vibrational and rotational quantum numbers of KBr** change by several tens during a single collision. Further, the large changes in the internal quantum numbers occur with appreciable probability. For example, during a collision with Ar at a c.m. scattering angle of 75°, the probability of KBr acquiring a c.m. recoil velocity of 1 km/s is about $\frac{1}{4}$ as large as the probability of having a near elastic c.m. recoil velocity of 0.2 km/s. The corresponding ratio at a c.m. scattering angle of 45° is about $\frac{1}{10}$. It is not possible to reconcile these observations with the existing theories [1]. Three-dimensional classical trajectory calculations using various potential-energy surfaces underestimate highly inelastic scattering of KBr** by Ar [7].

Relaxation of the vibrational degree of freedom, simply called the VT process, is described by the Landau-Teller [1,8] model. This model for atom-diatom collisions approximates the atom-diatom interaction potential by the sum of the atom-atom potentials. In addition, it assumes that the time duration of the collision is much smaller than the period of internal motion. Both these assumptions are well known to the students of scattering theory as the impulse approximation (IA). LT is a one-dimensional model in which rotations play no role. This model, of course, cannot be used to calculate differential cross sections. In this Brief Report we show how an exact IA calculation developed earlier [9] can be used to theoretically calculate the differential cross sections measured by Fisk and co-workers [2–5].

The impulse approach, as formulated by Chew and co-workers [10–12] has been applied to the vibrational-rotational excitation of a diatom during its collision with energetic atoms by Bogan [13], Eckelt and co-workers [14-17], and Beard and Micha [18]. The basic premises of the IA have already been mentioned. It has been shown by the present authors that the resulting equations can be solved exactly [9] without resorting to the peaking approximation. One benefit of the exact solution, in contrast to the peaking approximation where the two-body t matrix is evaluated for a given value of the spectator momentum and which had been used in all of the earlier atom-diatom studies [13–18], is that the relative momentum $\mathbf{p}_3$ and the intramolecular momentum due to

vibrational-rotational motion q_3 enter the formulation on an equal footing. This permits a solution of the problem where the collision energy is provided by the vibrational-rotational motion of the diatom rather than the relative translational energy of the atom-diatom motion. The expression for the differential cross section is given elsewhere [9] and will not be repeated here. We use a hard-core potential to represent the atom-atom interaction. For the internal energies under consideration the lowest state of KBr is ionic [19]. We approximate the Ar-K^+ and Ar-Br^- hard-core radii by the corresponding values for Ar-Ar and Ar-Kr, respectively. The latter parameters were taken from Hirschfelder, Curtiss, and Bird [20]. The sensitivity of the calculation to this approximate potential is discussed later. Having selected the potential we carry out an exact impulse calculation [9]. The KBr** wave functions were obtained using a potential function constructed from spectroscopic constants [21] and extrapolation by a Padé [2,2] approximant [22], adding the centrifugal term to obtain the effective potential-energy curve.

Figure 1 is a plot of the differential scattering cross section (cm^2/ sr), at a c.m. scattering angle of 75°, for vibrationally elastic scattering of KBr ($v=90$, $j=126$) by Ar, as a function of j' (solid circles). Also shown are the contributions to the cross section by collision of Ar with Br^- (squares) and K^+ (triangles). In addition to the peak due to elastic scattering, the Ar-Br^- cross section shows supernumerary rotational rainbows and a rotational rainbow [23] at $j'=70$. The cross section for scattering of K^+ alone by Ar gradually decreases from the peak at elastic scattering. The scattering amplitudes from the two scattering centers interfere constructively for even Δj and destructively for odd Δj. This interference as well as the rotational rainbows give rise to the complicated pattern for the variation of the differential cross section (solid circles) for the Ar-KBr system. It should be noted that the scattering from K^+ dominates for large Δj while the scattering from Br^- makes a larger contribution for smaller Δj. This is entirely appropriate since K^+ is farther from the c.m. of the molecule than is Br^- and a given change in the relative momentum leads to greater torque during a collision of Ar with K^+. Near the elastic peak the scattering from Br^- dominates because of the larger Br^--Ar hard-core collision diameter. The cross section drops sharply when j' exceeds 140 because the available translational energy is almost used up. The differential cross section at the c.m. scattering angle of 45° shows modulations similar to those observed at 75°. The only difference is that the rotational rainbows appear at smaller values of Δj. Again, this is reasonable because a given change in the linear momentum produces a larger torque at 75° than at 45°.

Figure 2 gives the same plot as in Fig. 1 for the final vibrational level 50. The theory of rainbows for the vibrational-rotational transitions is under development [24]. The structure of the differential cross section as a function of j' is understandably more complicated than that found in the very instructive earlier [23] study of rotational rainbows in the vibrationally elastic situation. The Ar-K^+ differential cross section clearly shows several supernumerary rainbows and a rainbow at $j'=240$. The reason for large variations in the differential cross section in the $j'=80$ to 130 region for the Ar-Br^- system and almost no variations at all for the Ar-K^+ system is not yet completely understood. It appears related to the fact that for a given change in the rotational quantum number a larger change in the quantum number for the orbital motion, and a greater change in the phase, is required for the Ar-Br^- collision than for Ar-K^+ collision. The scattering from K^+ again makes the dominant contribution to the cross section for large changes in j. Also, even for small changes in the rotational quantum number the scattering from K^+ is not much smaller than the scattering from Br^-. It is also seen that, compared to the vibrationally elastic scattering, the differential cross section is only smaller by less than a factor of about 10 for $v'=50$ when about 40% of the vibrational energy is converted into translational energy of relative motion. Our model reproduces the exper-

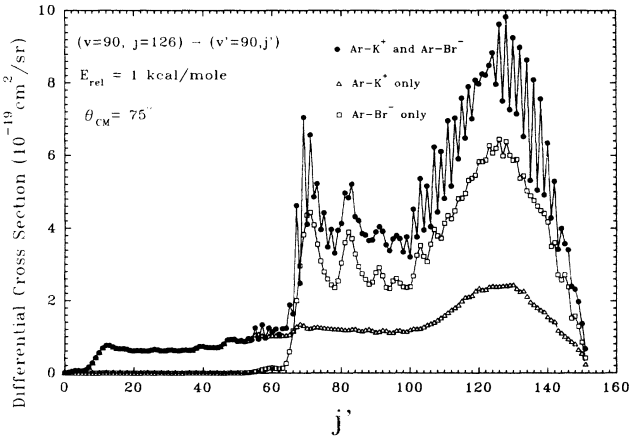

FIG. 1. Calculated differential cross section for scattering of KBr ($v=90$, $j=126$) by Ar with a relative translational energy of 1 kcal/mole at a center-of-mass (c.m.) scattering angle of 75° and final vibrational quantum number $v'=90$ as a function of the final rotational quantum number (j').

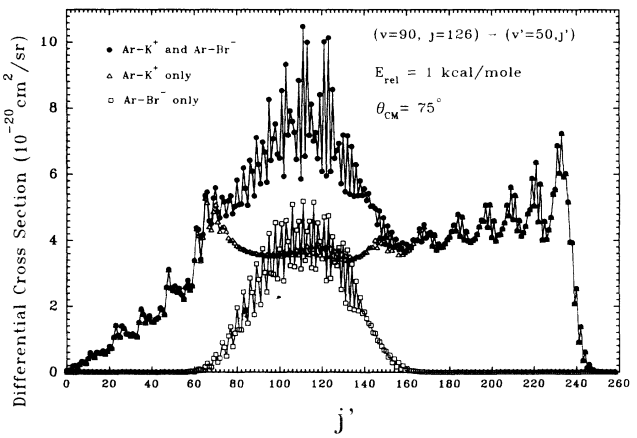

FIG. 2. Calculated differential cross section for scattering of KBr ($v=90$, $j=126$) by Ar with a relative translational energy of 1 kcal/mole at a c.m. scattering angle of 75° as a function of the final rotational quantum number (j') for $v'=50$ ($\Delta v=-40$).

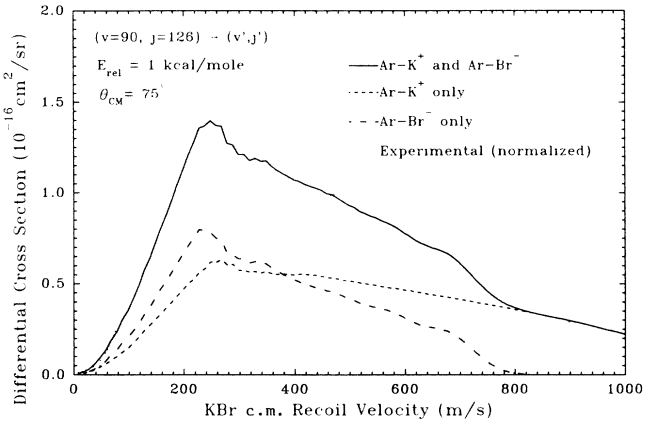

FIG. 3. Calculated and measured differential cross section for scattering of KBr ($v=90$, $j=126$) by Ar with a relative translational energy of 1 kcal/mole at a c.m. scattering angle of 75° as a function of the c.m. recoil velocity of KBr. The peak of the measured cross section is normalized to agree with the peak of the calculated cross section. The hard-core radii used are 3.40 Å for K^+-Ar and 3.85 Å for Br^--Ar. The four curves plotted are (i) Experimental measurements (dotted line), (ii) Ar-KBr calculation (solid line), (iii) Ar-K^+ calculation (dashed line), and (iv) Ar-Br^- (dash-dotted line).

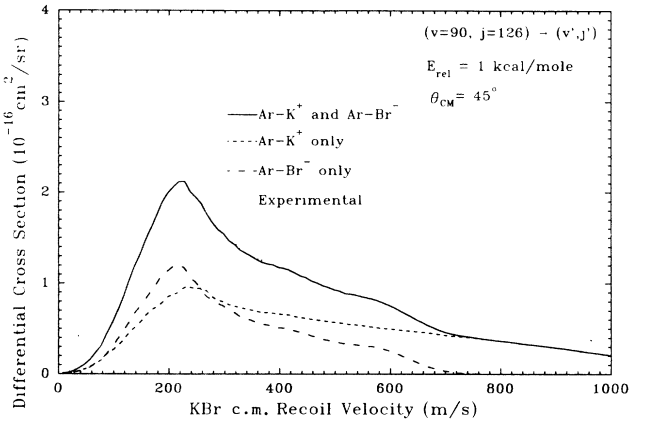

FIG. 4. Same as in Fig. 3 except the c.m. scattering angle is 45°. The cross sections plotted are now absolute. The normalization is taken from Fig. 3.

imental observation that the large vibrational quantum number changes take place with significant probability. For the c.m. scattering angle of 45°, the scattering from Br^- may be neglected.

Figure 3 is a plot of measured and calculated differential cross sections as a function of KBr recoil velocity in the c.m. system for a c.m. scattering angle of 75°, the largest scattering angle for which measurements are available. The calculated differential cross sections in this figure as well as in the previous ones took K^+-Ar and Br^--Ar hard-core radii to be 3.40 and 3.85 Å, respectively. The maximum of the measured relative differential cross section is normalized to agree with the peak of the calculated cross section. The calculated differential cross sections were averaged over an interval of 50 m/s of the KBr c.m. recoil velocity. The agreement between the calculation and the experiment is remarkable. Also shown in Fig. 3 are the results due to scattering by K^+ alone and Br^- alone. For nearly elastic collisions scattering due to Br^- makes a larger contribution while for highly inelastic collisions (the ones with large KBr recoil velocity), only the contribution from K^+ is important. When the K^+-Ar and Br^--Ar hard-core radii are taken to be 4.81 and 5.44 Å, respectively, only the magnitude of the calculated differential cross section changes; the shape of the curve for the differential cross section as a function of the KBr recoil velocity remains unchanged. Similar results were obtained when the two hard-core radii were taken to be 3.40 and 5.44 Å.

Figure 4 gives a plot of the differential cross section as a function of the KBr recoil velocity for the c.m. scattering angle of 45°, the smallest angle for which the experimental observations are available. The curves plotted are for scattering of Ar by KBr,K^+,Br^- as well as the experimentally observed results. Now the comparison between the calculations and measured results is absolute, the normalization factor being determined in Fig. 3. Highly inelastic collisions are again well described as due to scattering of Ar by K^+ alone. Nearly elastic scattering is underestimated by the calculation. This appears to be due to using a very simple model potential and ignoring the attractive part of the atom-ion potentials. This may also be the reason that the dip in the differential cross section at about 350 m/s KBr recoil velocity is not reproduced by the calculation.

In summary our model of the relaxation of highly internally excited KBr** during collision with Ar yields good agreement with the measured values at a c.m. scattering angle of 75°. The comparison with the experimental measurements for a 45° c.m. scattering angle yields good agreement for large KBr recoil velocity, while the calculation underestimates the nearly elastic experimental results by a factor of about 1.5. This is probably due to the neglect of the long-range attractive potential, which plays an important role for near elastic scattering at small c.m. scattering angles. Finally, because there are so many closely spaced final states involved in the calculation, the KBr recoil velocity distribution as a function of the calculated differential cross section is dependent only on the relative magnitudes and not on the shape of the state-to-state differential cross sections. This, we believe, makes the shape of the calculated KBr recoil velocity distribution rather insensitive to the hard-core parameters used.

Thus an application of the IA to a situation where the collision energy is provided by the internal motion of the target also marks an explanation of the observed rapid deactivation of highly excited KBr**.

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