



28 November 1997

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 280 (1997) 1–4

Threshold phenomena in ultracold atom–molecule collisions

N. Balakrishnan, R.C. Forrey, A. Dalgarno

Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA

Received 24 July 1997; in final form 25 August 1997

Abstract

Vibrational relaxation cross sections for an atom–molecule collision are calculated by explicit numerical solution of the coupled equations of scattering theory and shown to follow an inverse velocity dependence at very low initial kinetic energies of the incident atom, in accordance with Wigner's threshold law. Rate constants for $\text{H} + \text{H}_2(v, j = 0) \rightarrow \text{H} + \text{H}_2(v' < v, j = 0)$ are calculated for all the vibrational levels of H_2 and found to vary by seven orders of magnitude between the deepest level $v = 0$ and the vibrational level $v = 12$. © 1997 Elsevier Science B.V.

Following the success of experiments on trapping ultracold atoms, several schemes have been advanced for creating aggregates of ultracold molecules [1–5]. This would provide an opportunity for ultrahigh resolution spectroscopic investigations of long range molecular interactions and perhaps, development of novel molecular beam sources [2,4]. Many of the proposed schemes involve preparing trapped molecules with significant thermal [1,3] or nonthermal vibrational excitation. The translationally cold, vibrationally hot molecules thus prepared thermalize to 250 mK by ^3He collisions [1,3] or to 500 μK by ultracold alkali atom collisions [2], and are eventually trapped in a far-off resonance trap (FORT) [2,3] or magnetic trap [1]. To maximize the density of the cold molecules, it is desirable to restrict other processes by which they would be lost from the region in which they are produced [1,2]. If the rate coefficients for the exoergic inelastic or reactive collisions with the cold atoms are large, collisions could have an adverse effect as the excess energy liberated heats the cold atoms and molecules, and may eject them from the trap [2]. According to Wigner's threshold

law [5], the rate coefficients for quenching are finite at zero temperature but are usually believed to be small. We show here that on the contrary for collisions of H with H_2 , the rate coefficients for the quenching of high vibrational levels are large.

The magnitude of collisional quenching is determined by the intermolecular forces between the cold atoms and the molecules. Quantum mechanical effects play a dominant role at low energies, and the scattering becomes sensitive to fine details of the interaction potential. For processes which do not require any activation energy, the cross sections and rate constants can exhibit quite different behavior at low energies compared to thermal energies. An example is the collisional relaxation of a vibrationally excited diatomic molecule by an atom. For such a system, the internal energy of the molecule in the entrance channel (E_i) is larger than in the exit channel (E_j). At the threshold of the entrance channel the exit channel is open and the difference in internal energy $E_i - E_j$ appears as kinetic energy in the outgoing channel. This exothermic process is sometimes referred to as *superelastic scattering*. The

corresponding relaxation cross section tends to infinity in the limit of zero kinetic energy of the incoming atom according to Wigner's threshold laws [6].

Though asymptotic forms of quantum mechanical threshold laws may be derived rigorously, their validity or importance for actual molecular systems is difficult to establish. Previous studies of threshold effects on molecular systems have focused on vibrational relaxation of van der Waals complexes such as $\text{He} \cdots \text{I}_2$ [7–9], unimolecular rearrangement of weakly bound complexes of $\text{H} \cdots \text{H}_2/\text{D}_2$, and bimolecular chemical reactions in $\text{H} + \text{H}_2/\text{D}_2$ systems [10,11]. These studies have been limited to a small number of vibrational levels and no systematic investigation of the threshold effects as a function of vibrational quantum number of the molecule has been reported.

Here, we examine the threshold behavior of *superelastic scattering* events by carrying out quantum mechanical calculations on an accurate Born–Oppenheimer potential energy surface (PES) [12]. We consider $\text{H} + \text{H}_2(v) \rightarrow \text{H} + \text{H}_2(v' < v)$ where v is the vibrational level quantum number. Since the kinetic energy in the incoming channel is nearly zero, only the incident $l = 0$ partial wave needs to be considered. To keep the problem simple and the results more transparent, we assume that the molecule is initially and finally in the $j = 0$ rotational level in the various vibrational states.

The total wave function of the system is expanded in terms of ro-vibrational eigenfunctions of the diatomic molecule in the total angular momentum representation of Arthurs and Dalgarno [13] and the resulting coupled equations for the radial motion obtained from the time-independent Schrödinger equation are solved using the general inelastic scattering program MOLSCAT [14]. The diatomic vibrational wave functions used for generating the coupled equations are obtained as expansions in Hermite polynomials. For the highest bound state, ($v = 14$) the energy is converged to better than 1 cm^{-1} . Because the $\text{H} + \text{H}_2$ system is very strongly coupled, we used the quasi-adiabatic modified log derivative method of Manolopoulos [15] to solve the coupled equations.

Fig. 1 shows the vibrational relaxation cross sections for different initial vibrational states $v = 1, 3, 5$ and 14 as a function of the kinetic energy of the

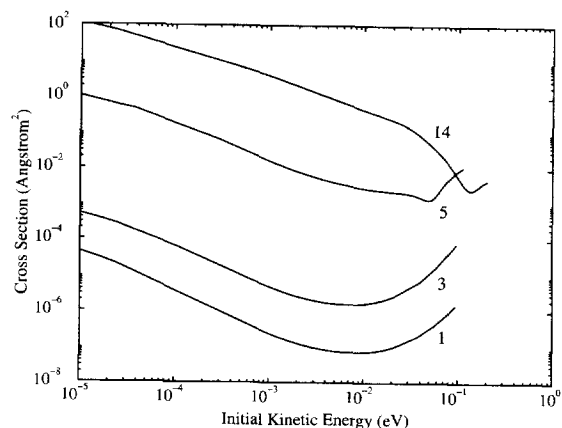


Fig. 1. The vibrational relaxation cross sections for $\text{H} + \text{H}_2(v, j=0) \rightarrow \text{H} + \text{H}_2(v-1, j=0)$ for different initial vibrational levels (v) as a function of the incident kinetic energy of the H atom; the curves are labeled by the initial vibrational quantum number.

atom for energies below 0.1 eV. At these energies, only *s*-wave scattering in the incident channel contributes. In the numerical calculations, we were careful to ensure that the interaction potential matrix elements at the matching point were negligible compared to the energy of the incoming wave. Each of the cross sections decreases initially as the velocity is decreased and passes through a minimum before exhibiting the threshold behavior predicted by Wigner's law. For energies below 10^{-3} eV , the cross sections vary as $1/k$ where k is the wave number for the incident channel. The region of applicability of Wigner's law extends to higher energies as v increases. The cross sections for v between 1 and 14 differ by six orders of magnitude in the energy range where Wigner's threshold law holds. We have included the coupling between all the discrete vibrational levels but have omitted coupling to the closed vibrational continuum. This coupling is likely to be important for $v \geq 6$ [16] and our calculated values become less accurate. We present values for $v = 9, 12$ and 14 nevertheless, because they provide a useful indication of the possible magnitude of the rate coefficients for the high vibrational levels that may be accessed in experiments on ultracold molecules. The accuracy of the predicted rate coefficients is also limited by the neglect of rotational coupling and reactive scattering.

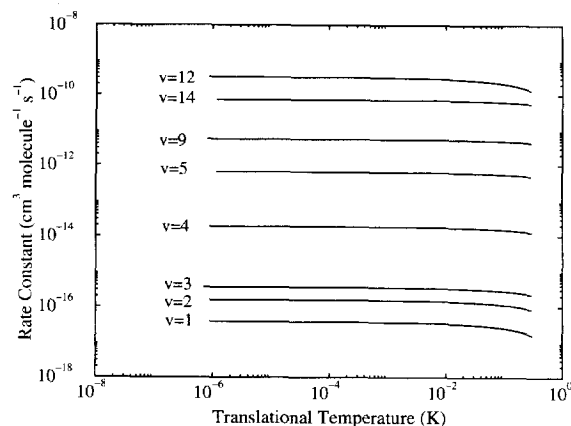


Fig. 2. Single quantum vibrational deactivation rate coefficients for H_2 as a function of translational temperature. The curves are labeled by the initial vibrational quantum number of the molecule.

The quenching rate coefficients tend to finite values at low temperatures. Single quantum relaxation rate coefficients for the vibrational levels $v = 1$ to 5 and $v = 9, 12$ and 14 of H_2 are shown in Fig. 2. The rate coefficients are independent of temperature below 10^{-2} K. The smallest rate coefficient is $10^{-17} \text{ cm}^3 \text{ s}^{-1}$ for the transition from $v = 1$ to $v = 0$ and the largest $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $v = 12$ to $v = 11$. In Fig. 3 we present rate coefficients for $\Delta v = 2$ transitions from initial vibrational levels $v = 2$ to 5 and $v = 9, 12$ and 14. The double quantum transition rates are smaller than the single quantum relaxation

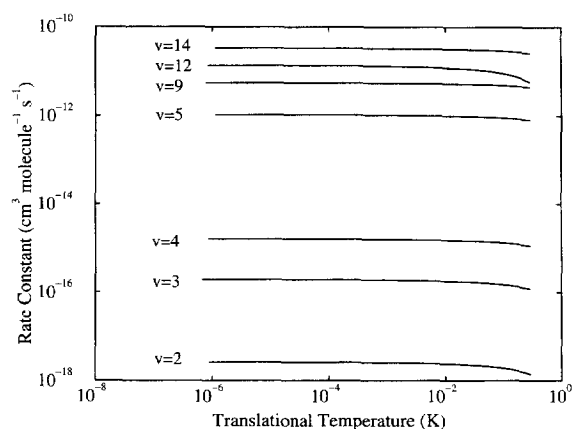


Fig. 3. Double quantum vibrational deactivation rate coefficients for H_2 as a function of translational temperature. The curves are labeled by the initial vibrational quantum number of the molecule.

rates except for $v = 5$ for which the former is a factor of about 1.6 larger and for $v = 9$ for which both are comparable in magnitude. For $v > 5$, the magnitude of the $\Delta v = 3$ and other multiquantum transitions which involve the exchange of several vibrational quanta are also within the same order of magnitude as that of $\Delta v = 2$ or in certain cases $\Delta v = 1$ transitions. Such distributions of final vibrational levels have been previously reported for the present system [16] and for the deactivation of vibrationally excited N_2 molecules in $\text{N} + \text{N}_2$ collisions at elevated temperatures [17]. A more detailed analysis of the vibrational multiquantum transitions and the effect of coupling the closed continuum channels will be reported separately.

The dramatic variation of the rate coefficients with v and the large values for the high vibrational levels can be explained in terms of the matrix elements of the interaction potential between the vibrational wave functions as a function of the atom–molecule relative center of mass separation R . The spherically symmetric part of the interaction potential matrix elements between v and $v - 1$ states are shown in Fig. 4 for both low and high vibrational levels. For vibrational levels below $v = 5$, the interaction is localized within a short range of R and vanishes rapidly as R is increased. For higher v states, the molecule is stretched and the matrix elements are significant over an extended range of R .

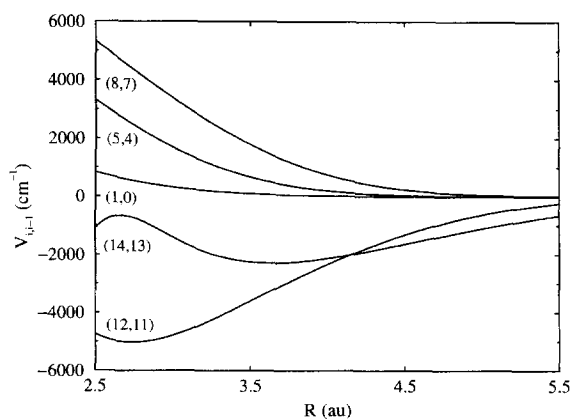


Fig. 4. Interaction potential matrix elements between adjacent vibrational levels as a function of the radial coordinate. The numbers within parentheses for each curve indicate the initial and final vibrational levels.

Vibrational transitions can be induced only if the incoming wave penetrates into the region of strong coupling. The small quenching rates for the low vibrational levels indicate that this does not happen at low velocities. For high vibrational levels, the extended coupling along the radial coordinate causes a large perturbation of the incoming wave even at large R values.

In an earlier study of vibrational quenching in the Wigner limit, Schwenke and Truhlar [8] calculated cross sections for the $v = 16 \rightarrow 15$ and $1 \rightarrow 0$ transitions in I_2 due to collisions with He and obtained a ratio of 20.5. The present study has demonstrated that vibrational relaxation of a molecule can be very efficient in collision with a cold atom and it depends strongly on the initial vibrational level of the molecule. For $H + H_2(v)$, the relaxation rate coefficients vary by seven orders of magnitude between $v = 1$ and $v = 12$. The efficient quenching of higher vibrational levels may impose limits on the densities that can be achieved in some schemes for producing ultracold molecules but may increase the effectiveness of others. Their role in the actual experiments will depend on the system under investigation and the precise nature of the intermolecular forces.

Acknowledgements

These calculations were initiated in response to queries about vibrational quenching efficiencies at low temperatures from Dr. D. Kleppner and Dr. R.G. Hulet. We thank Dr. H. Friedrich for stimulating discussions and Dr. W.C. Stwalley for his instructive

comments on an earlier draft. This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Office of Energy Research (RCF), and by the National Science Foundation, Division of Atmospheric Science (NB).

References

- [1] J.M. Doyle, B. Friedrich, J. Kim, D. Patterson, *Phys. Rev. A* 52 (1995) R2515.
- [2] Y.B. Band, P.S. Julienne, *Phys. Rev. A* 51 (1995) R4317.
- [3] B. Friedrich, D.R. Herschbach, *Phys. Rev. Lett.* 74 (1995) 4623.
- [4] J.T. Bahns, W.C. Stwalley, P.L. Gould, *J. Chem. Phys.* 104 (1996) 9689.
- [5] R. Côté, A. Dalgarno, *Chem. Phys. Lett.*, in press.
- [6] E.P. Wigner, *Phys. Rev.* 73 (1948) 1002.
- [7] W.R. Gentry, *J. Chem. Phys.* 81 (1984) 5737.
- [8] D.W. Schwenke, D.G. Truhlar, *J. Chem. Phys.* 83 (1985) 3454.
- [9] S.K. Gray, S.A. Rice, *J. Chem. Phys.* 83 (1985) 2818.
- [10] G.C. Hancock, C.A. Mead, D.G. Truhlar, A.J.C. Varandas, *J. Chem. Phys.* 91 (1989) 3492.
- [11] T. Takayanagi, N. Masaki, K. Nakamura, M. Okamoto, G.C. Schatz, *J. Chem. Phys.* 86 (1987) 6133.
- [12] A.I. Boothroyd, W.J. Keogh, P.G. Martin, M.R. Peterson, *J. Chem. Phys.* 104 (1996) 7139.
- [13] A.M. Arthurs, A. Dalgarno, *Proc. Roy. Soc. Lond. A* 256 (1963) 540.
- [14] J.M. Hutson, S. Green, MOLSCAT computer code, version 14 (1994), distributed by Collaborative Computational Project No. 6, Engineering and Physical Sciences Research Council, UK.
- [15] D.E. Manolopoulos, *J. Chem. Phys.* 85 (1986) 6425.
- [16] K. Onda, *J. Phys. B: At. Mol. Opt. Phys.* 24 (1991) 4509.
- [17] I. Armenise, M. Capitelli, E. Garcia, C. Gorse, A. Laganá, S. Longo, *Chem. Phys. Lett.* 200 (1992) 597.