Rovibrational quenching of BH in ultracold ^{3}He collisions*

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The interaction potential of a He–BH complex is investigated by the coupled-cluster single-double plus perturbative triples (CCSD (T)) method and an augmented correlation consistent polarized valence (aug-cc-pV)5Z basis set extended with a set of (3s3p2d1f1g) midbond functions. Using the five two-dimensional model potentials, the first three-dimensional interaction potential energy surface is constructed by interpolating along (r–r_e) by using a fourth-order polynomial. The cross sections for the rovibrational relaxation of BH in cold and ultracold collisions with ^{3}He atom are calculated based on the three-dimensional potential. The results show that the $\Delta v = -1$ transition is more efficient than the $\Delta v = -2$ transition, and that the process of relaxation takes place mainly between rotational energy levels with the same vibration state and the $\Delta j = -1$ transition is the most efficient. The zero temperature quenching rate coefficient is finite as predicted by Wigner's law. The resonance is found to take place around 0.1–1 cm^{-1} translational energy, which gives rise to a step in the rate coefficients for temperatures around 0.1–1 K. The final rotational distributions in the state $v = 0$ resulting from the quenching of state ($v = 1, j = 0$) at three energies corresponding to the three different regimes are also given.

Keywords: He–BH complex, potential energy surface, cold collision, cross section

PACC: 3430, 3450, 3450E

1. Introduction

Energy transfer processes in weakly interacting molecular systems have a bearing upon several areas of physical, chemical, and applied research. Currently, the possibility of creating coherent sources of molecular condensates similar to those of atomic Bose–Einstein condensates has aroused much interest in low energy atomic and molecular collisions. Several review papers have appeared recently.[1−4] Their potential applications are in such areas as ultrahigh resolution molecular spectroscopy, controlled chemical reactions, and determination of accurate intermolecular potentials.

In the past several years, alternative methods of cooling molecules directly have included photoassociation of ultracold atoms, buffer gas cooling, and Stark slowing. As a matter of fact, cold atom photoassociation or buffer-gas cooling generates translationally cold but vibrationally and rotationally excited molecules. The efficiency of cooling depends on the relative magnitude of elastic and inelastic scattering cross sections. So, in order to improve cooling and trapping efficiencies, theoretical studies of collisional quenching of rovibrational levels of trapped molecules, which may lead to trap loss, are needed.

In previous papers, there have been several studies of elastic and inelastic cold collisions of He atoms and diatomic molecules: He+H_2, He+O_2, He+CO, He+CaH, He+NH, He+F_2, He+N_2, etc.[5] These studies have shown that rovibrational energy transfer can be extremely efficient at ultracold temperatures and that it is sensitive to the initial rovibrational energy levels. It was shown that the energy transfer cross sections follow Wigner's laws at very low kinetic energies. It is sufficient to describe the collisions in terms of a complex scattering length whose imaginary part is directly related to the zero temperature value of the corresponding inelastic quenching rate coefficient.[6]

Considering the structures and dynamics of boron family hydrides with rare-gas atom complexes, there are only reports on Ar–BH and Ar–AlH complexes. In 1994 Hwang and Dagdigian reported on LIF spectra for the $A^1\Pi \rightarrow X^1\Sigma$ transitions of Ar–BH[7] and

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Ar–AlH.[8] In order to assist in the assignment of the vibronic structure, Alexander *et al.* calculated the potential energy surfaces (PESs) of Ar–BH ($A^1\Pi$, $X^1\Sigma$)[9] and Ar–AlH ($A^1\Pi$, $X^1\Sigma$)[10] complexes, respectively, using a multi-reference configuration interaction method (MR–CI(D)) with a quadruple zeta quality basis set (avqz-f). For both complexes, each PES yielded bent equilibrium structures for the ground and excited states. In the year 2000, Nizamov and Dagdigian reported on an experimental study of rotationally inelastic collisions of AlH($A^1\Pi$) with Ar atoms.[11] Bimolecular state-to-state and total removal rate constants were determined. The state-to-state rate constants displayed dramatic Λ-doublet propensities.

In 2007, we investigated accurately a two-dimensional intermolecular ground state potential of a He–BH complex.[12] The potential was used to calculate elastic, inelastic and total differential cross sections for collisions between the He atom and the ground state of the BH molecule by Wang *et al.* in 2009.[13] In the present work, we keep investigating the rovibrational relaxation at cold temperatures, including the relative efficiency of the double and single vibrational quantum de-excitation processes, the translational energy dependences of cross sections and rate coefficients, and the final rotational distributions. To our knowledge, there is as yet no report in these areas.

The rest of the present paper is organized as follows. In Section 2, we present a three-dimensional PES of the He–BH system. In Section 3, the method and the parameters used to make the scattering calculations are briefly discussed. Results and discussion are given in Section 4.

2. Computational method

2.1. Three-dimensional PES of the He−BH system

In order to accurately describe the weak interaction between He and BH molecules, the use of large basis sets and the inclusion of high-order electron correlation effects are needed. In this work, an augmented correlation consistent polarized valence aug-cc-pV5Z basis set extended with a (3s3p2d1f1g) midbond function is used in the coupled-cluster single-double plus perturbative triples (CCSD(T)) calculation.[12] Jacobi coordinates (r, R, θ) are used throughout the present work. Here, r is the distance between the BH molecules, R is the distance between the He atom and the centre of mass of the BH diatom, and θ is the angle between r and R. The calculations are carried out over five values of B–H distance r: {1.90651, 1.98589, 2.32909, 2.82081, 3.00482} a_0, 18 values of the intermolecular separation R: {5.0, 5.5, 5.8, 6.0, 6.25, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10, 11, 12, 13, 14, 15}a_0, and 12 values of angle θ: {0, 15, 30, 45, 60, 70, 80, 100, 120, 140, 160 and 180°}, resulting in the PES consisting of a total of 1080 configurations. All the calculations are carried out using the Molpro 2006 package.

We investigate the rovibrational quenching of BH with He. So a complete three-dimensional PES $V(r, R, \theta)$ must be constructed. The method of constructing a three-dimensional PES can be found in our recent papers.[12,14−16] Speaking briefly, the three-dimensional PES is constructed by two steps. In the first step, for each value of $r_{\rm BH}$ = 1.90651a_0, 1.98589a_0, 2.32909a_0, 2.82081a_0, 3.00482a_0, the interaction energies in R and θ are fitted to a two-dimensional PES by using the potential model proposed by Bukowski *et al.*[17] and used by other researchers.[18] In the second step, the five two-dimensional PESs obtained in the first step are then used to construct the 3D PES by interpolating along $(r–r_{\rm e})$ through using a fourth-order polynomial. The total root-mean-square (RMS) error is 0.03 $\rm cm^{-1}$ and the maximum absolute deviation is 0.09 $\rm cm^{-1}$. A FORTRAN subroutine for generating the full three-dimensional PES is available on request.

2.2. Scattering calculation

The quantum mechanical scattering calculations are carried out by the close-coupling method.[19,20] The atom–diatomic Hamiltonian in the centre-of-mass frame is given by

$$H = -\frac{1}{2m}\nabla_r^2 - \frac{1}{2\mu}\nabla_R^2 + v(r) + V_I(r, R, \theta), \quad (1)$$

where m is the reduced mass of the diatomic molecule, and μ is the reduced mass of the He atom with respect to the diatomic molecule. The full wave function is expanded in a set of channel functions ($n \equiv vjl$),

$$\psi^{JM}(\boldsymbol{R}, \boldsymbol{r}) = \frac{1}{R}\sum_n C_n(R)\phi_n(\hat{R}, \boldsymbol{r}), \quad (2)$$

$$\phi_n(\hat{R}, \boldsymbol{r}) = \frac{1}{r}\chi_{vj}(r)\sum_{m_j}\sum_{m_l}(jlJ|m_j, M-m_l) \times Y_{m_j}^j(\hat{r})Y_{m_l}^l(\hat{R}), \quad (3)$$

where l is the orbital angular momentum of BH, J is the total angular momentum of the He–BH complex, M is the projection of J onto the space-fixed z axis, $(jlJ\,|m_j, M-m_l)$ denotes a Clebsch–Gordon coefficient, and $\chi_{vj}(r)$ is the rovibrational wave function of the BH molecule. The potential curve of the BH molecule is also calculated by the CCSD(T) method extended with the aug-cc-pV5Z basis set. The equilibrium value and the spectroscopic constants $\omega_{\rm e}$ and $\omega_{\rm e}\chi_{\rm e}$ are in good agreement with experimental values.

The interaction potential $V_{\rm I}$ is expanded in Legendre polynomials as follows:

$$V_{\rm I}(R,r,\theta) = \sum_{\lambda=0}^{\infty} V_\lambda(R,r)\mathrm{P}_\lambda(\cos\theta). \tag{4}$$

Operating the Hamiltonian (1) on channel function (2) leads to a set of coupled equations that can be solved by the R-matrix method.

The cross sections and the rate coefficients are respectively given by

$$\begin{aligned}&\sigma_{vj\to v'j'}\\ &= \frac{\pi}{2\mu E_j(2j+1)}\sum_J^{\infty}(2J+1)\\ &\quad\times\sum_{l=|J-j'|}^{|J+j|}\sum_{l'=|J-j'|}^{|J+j'|}\left|\delta_{jj'}\delta_{ll'}\delta_{vv'}-S^J_{vjl;v'j'l'}\right|^2, \end{aligned}\tag{5}$$

$$\begin{aligned}&R_{vj\to v'j'}(T)\\ &= (8K_{\rm B}T/\pi\mu)^{1/2}\frac{1}{(K_{\rm B}T)^2}\int_0^{\infty}\sigma_{vj\to v'j'}(E_K)\\ &\quad\times\exp(-E_K/K_{\rm B}T)E_K\,\mathrm{d}E_K. \end{aligned}\tag{6}$$

The total quenching rate coefficients are given by

$$R_{vj}(T) = \sum_{v'j'} R_{vj\to v'j'}(T). \tag{7}$$

The meaning of various variables and symbols can be found in Ref. [19].

In the limit of zero kinetic energy, it is convenient to express the scattering cross section in terms of the scattering length ($a_{vj} = \alpha_{vj} - \mathrm{i}\beta_{vj}$). The elastic cross section becomes finite in the zero energy limit and its magnitude is given by

$$\sigma_{vj\to v'j'} = 4\pi(\alpha_{vj}^2+\beta_{vj}^2) \approx 4\pi\alpha_{vj}^2, \tag{8}$$

and the zero temperature quenching rate coefficient is given by

$$\lim_{T\to 0} R_{vj}(T) = \frac{4\pi\hbar\beta_{vj}}{\mu}. \tag{9}$$

In the limit of zero temperature, Wigner's law holds and the quenching rate coefficients attain finite values.

3. Results and discussion

We have used the R-matrix method to solve the coupled-channel Schrödinger equation. Three vibrational channels ($v = 0, 1, 2$) are included in the calculations and a maximum value of $j = 13$ is allowed for each level of the vibrational manifold.

In Fig. 1 we report on the quenching cross sections of $v = 2 \to v' = 1$ and $v = 2 \to v' = 0$ each as a function of relative kinetic energy. The single jump cross section is orders of magnitude larger than the double jump one. Thus, the total quenching cross sections are almost completely determined by the single jump process. The resonances are also found to occur in the region of 0.1–1 cm^{-1} translational energy.

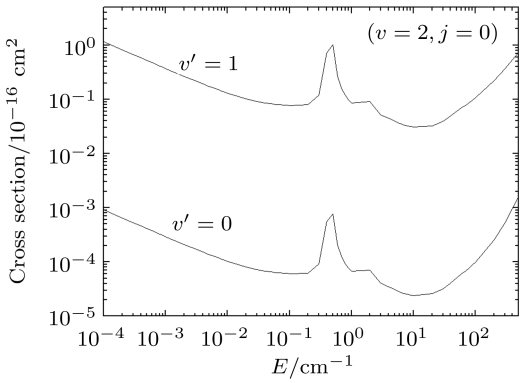


Fig. 1. Quenching cross sections of BH ($v = 2, j = 0$) by ^{3}He as functions of kinetic energy for $\Delta v = -1$ and $\Delta v = -2$ vibrational transitions.

Further, we compare the single jump de-excitation cross section of $v = 2 \to v' = 1$ with that of $v = 1 \to v' = 0$ in Fig. 2. The quenching curves of two transitions have a similar structure, but the former is about three times higher than the latter in the ultra-low energy region. The quenching is more efficient for the higher vibrational manifold for the BH and ^{3}He collision system.

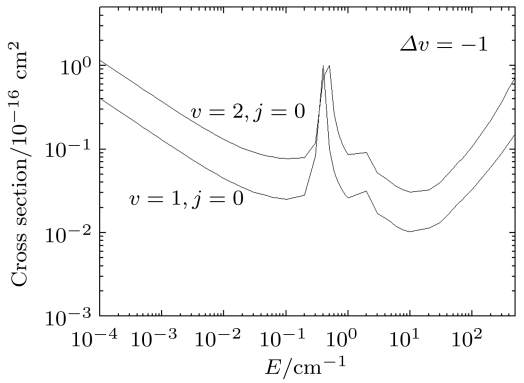


Fig. 2. Quenching cross sections of BH ($v = 2, j = 0; v = 1, j = 0$) by ^{3}He as functions of kinetic energy for $\Delta v = -1$ vibrational transitions.

The corresponding rate coefficients are presented in Fig. 3. The low temperature quenching rate coefficients for the states $(v = 1, j = 0)$ and $(v = 2, j = 0)$ are on the order of 10^{-19} cm^3/s, and the quenching rate coefficient for the higher vibrational manifold is larger than that for the lower vibrational manifold. For the state $(v = 2, j = 0)$, the quenching rate coefficient exhibits a maximum around 0.5 K. Similarly for the state $(v = 1, j = 0)$, a maximum occurs around 0.4 K. The humps in the quenching rate coefficient curves in a temperature range of 0.3–0.6 K are due to the contributions from the shape resonances shown in Fig. 2. When the temperature varies from 0.4 K to 0.01 K, the quenching rate coefficient presents a dropping tendency. But when the temperature continues to decrease, the quenching rate coefficient curve becomes flat and the quenching rate coefficient tends to be a finite value, which accords with Wigner's law. The corresponding elastic rate coefficient decreases when the temperature reduces and is two orders of magnitude larger than the quenching rate coefficient, which is of benefit to the reduction of the trapping loss and to further cooling by vapouring means.

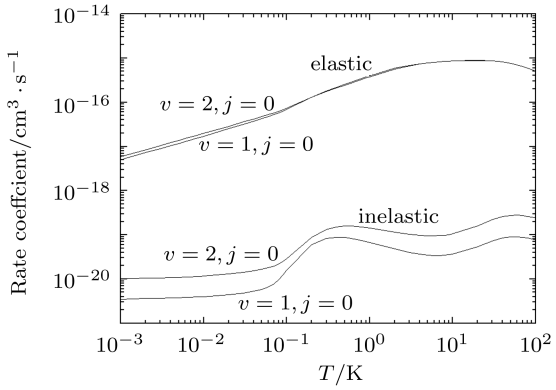


Fig. 3. Rate coefficients of the $(v = 1, j = 0; v = 2, j = 0)$ level of BH in collisions with ^{3}He as functions of temperature.

Figure 4 shows the cross sections of the $(v = 1, j = 8)$ state of BH. The total inelastic cross sections are given by

$$\sigma_{v=1,j=8} = \sum_{j'=0}^{7} \sigma(v = 1, j = 8 \to v' = 1, j') + \sum_{j'=0}^{7} \sigma(v = 1, j = 8 \to v' = 0, j').$$

We find the usual profile as a function of energy for similar van der Waals complexes with a very low energy Wigner regime. When the kinetic energy is less than 0.1 cm^{-1}, the elastic cross sections tend to be constant values but the inelastic cross sections increase linearly with the decrease of kinetic energy. On the other hand, the elastic cross sections are larger than the total inelastic cross sections. As can be seen, the elastic cross section is about 4 times larger than the total inelastic cross section when the kinetic energy is around 10^{-4} cm^{-1} and the former is about 100 times larger than the latter at near 1 cm^{-1}. This scenario is of benefit to cooling and trapping molecules. By comparing the sum of pure rotational cross sections for $v = 1, j = 8 \to v' = 1, j' \leq 7$ with the sum of vibrational cross sections for $v = 1, j = 8 \to v' = 0, j' \leq 7$ we can see that the former is five orders of magnitude larger than the latter in the whole range of energy considered. This shows that the vibrational quenching is quite small compared with the pure rotational quenching, which is due to the fact that the potential is weakly dependent on the BH stretching coordinate. We find that the sum of the pure rotational cross sections curve is almost coincident with the total inelastic cross section curve. Thus, the total inelastic cross sections are most completely determined by the pure rotational jump process. The resonances are also found to occur at about the translational energy (0.1–10 cm^{-1}). Similar structures are also found in Figs. 1, 2 and 5 separately. This results from the centrifugal barrier.

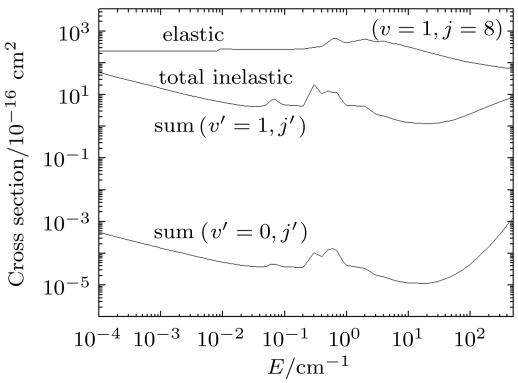


Fig. 4. Cross sections of BH $(v = 1, j = 8)$ by collision with ^{3}He as functions of kinetic energy.

In Fig. 5 we show the rotational quenching cross sections from the $(v = 1, j = 8)$ level of BH each as a function of kinetic energy. The cross section for $j = 8 \to j' = 7$ is the largest one. The process of relaxation takes place mainly between rotational energy levels with the same vibration states, and the $\Delta j = -1$ transition is most efficient.

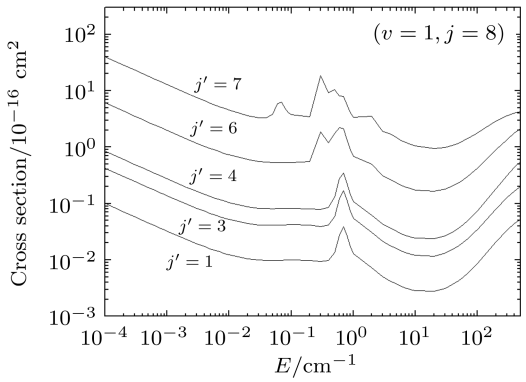


Fig. 5. Quenching cross sections of BH $(v = 1, j = 8)$ by collisions with ^{3}He as functions of kinetic energy.

In Fig. 6 we show the distributions of final rotational levels in the state $v = 0$ resulting from the quenching of $(v = 1, j = 0)$ state. We choose three energies corresponding to the Wigner, the van der Waals, and the high-energy regimes respectively. The distributions are similar. The distribution peaks appear near $j' = 7$ and $j' = 8$. The strength of the distribution at 10^{-4} cm^{-1} is greater than those at the other two energies (10 cm^{-1}, 500 cm^{-1}). The distribution reaches higher j levels as the energy increases which is modified because a number of higher angular momentum partial waves contribute at higher energies, thereby leading to a broader distribution of rotational levels.

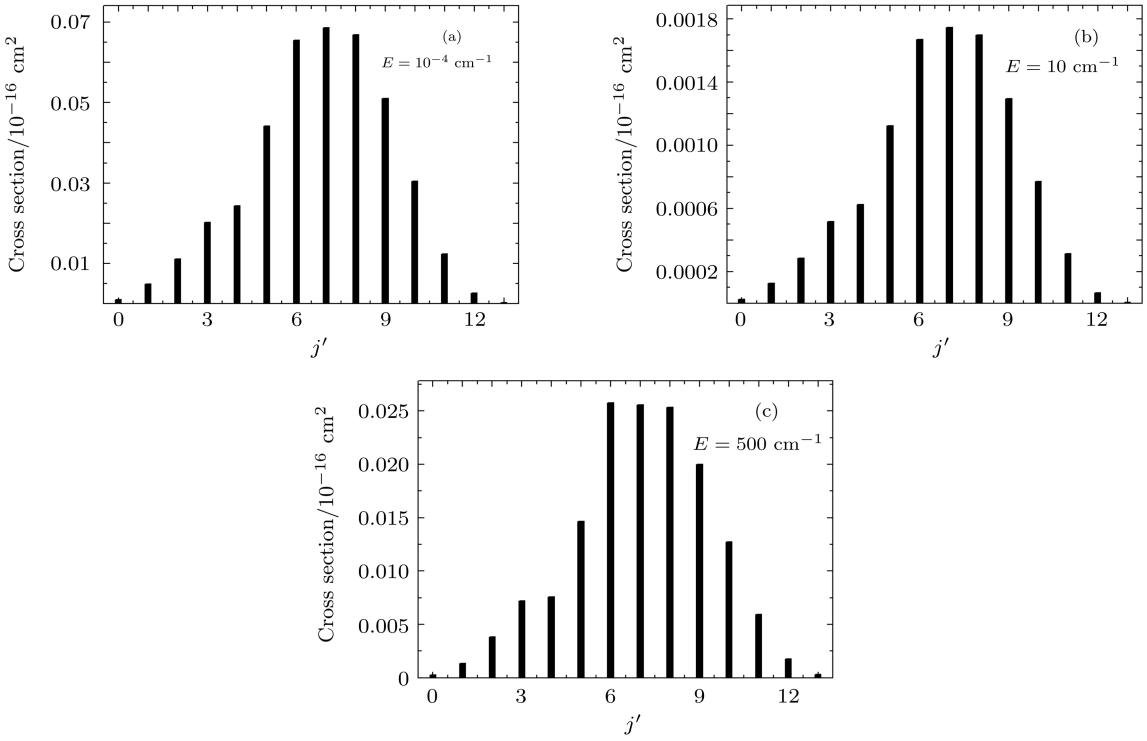


Fig. 6. Distribution of final rotational levels in $v = 0$ resulting from the quenching of the $(v = 1, j = 0)$ state of BH by collisions with He. The kinetic energies are 0.0001, 10 and 500 cm^{-1} which correspond to the Wigner, the van der Waals, and the high-energy regimes respectively.

4. Conclusions

We performed the calculation of PES for a He–BH complex. The CCSD(T) method and the aug-cc-pV5Z basis set extended with (3s3p2d1f1g) midbond functions are employed. Using the five two-dimensional model potentials, the first three-dimensional interaction potential energy surface is constructed by interpolating along $(r–r_e)$ by using a fourth-order polynomial.

Based on the three-dimensional PES, the relaxation of rovibration energy of BH in cold collisions with ^{3}He is studied in detail. The elastic cross sections are found to be a finite limiting value and the inelastic quenching cross sections are inversely proportional to the velocity of the incoming atom in the zero temperature limit, following Wigner's threshold law. We find that the $\Delta v = -1$ transition is more efficient than the $\Delta v = -2$

transition. The process of relaxation takes place mainly between rotational energy levels with the same vibration state and the $\Delta j = -1$ transition is most efficient. The zero temperature quenching rate coefficient is finite. Because there exists a centrifugal barrier, the resonance is also found to occur at about the translational energy (0.1–1 cm^{-1}), which gives rise to a step in the rate coefficients for temperatures around 0.1–1 K. The final rotational distributions in the state $v = 0$ resulting from the quenching of state $(v = 1, j = 0)$ at three energies corresponding to the three different regimes are given.

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