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低碰撞能下 Ne 原子对 LiH 分子转动猝灭的研究*

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摘 要：用密耦方法首次研究了 Ne 原子和 LiH 分子低能碰撞下的转动猝灭过程. 在碰撞能低于 10^{-4} cm^{-1}时，弹性截面趋于常数值，非弹性截面随碰撞速度减小线性增加，遵循 Wigner 定则预言的趋势. 对于一个给定的能量，总的猝灭截面是随着初始 j 的增加而减少的. 当能量在 0.01～100 cm^{-1}范围内，弹性和非弹性截面均比其它的体系表现出更复杂的振荡行为，这主要是由于体系具有强的各向异性以及它们具有两个吸引阱而造成的. 计算表明，在零温极限下，猝灭速率系数达到 10^{-11} $cm^3 s^{-1}$数量级. 当 $j=7$ 速率系数出现反转结构.

关键词：LiH 分子；低能碰撞；转动猝灭

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Rotational quenching of LiH by Ne at low energy

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Abstract: Rotational quenching of LiH by Ne at low energy is first studied using the close coupling approach. At incident energies below 10^{-4} cm^{-1}, the inelastic quenching cross sections are found to be inversely proportional to the velocity of the incoming Ne atom in agreement with Wigner threshold law, and the elastic cross sections are found to tend to constant limiting values. For a given energy, the total quenching cross sections decrease in general with increasing initial j. In the energy range $E_j = 0.01 - 100$ cm^{-1} the elastic and inelastic cross sections show more complicated oscillational behaviors than other studied systems, due to the stronger anisotropy and two attractive wells of the interaction potential. The calculations show the quenching rate coefficients attain their values of the order of 10^{-11} $cm^3 s^{-1}$ at zero temperature limiting. For $j=7$ the rate coefficient presents upturn structure.

Key words: LiH molecule, low energy collision, rotational quenching

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1 Introduction

In the last years, there is a very rapidly growing interest, both experimental and theoretical, in the field of cold molecules. Such a growth has been inspired by the spectacular results of Bose – Einstein condensation of ultracold atoms. The cooling and trapping of molecules is opening new perspectives in ultracold molecular physics and chemistry[1~6]. Its potential application involves high resolution molecular spectroscopy, coherent sources of molecular beams, and controlled chemical reactions. There are currently three experimental schemes that can be used to produce and trap cold molecules. One of the most widely used methods is cold atom photoassociation[1,2]. It produces the molecules in transitionally cold, rovibrationally hot states. The second involves buffer gas loading technique[3]. When the ^{3}He is employed, the temperature can be as low as 250 mK in a magnetic trap. The last method uses a time-varying electric field (Stark decelerator) to slow down neutral polar molecules and then trap them in electrostatic quadrupole trap or in electrostatic storage ring[4,5].

Regardless of the specific experimental and technical details adopted, it is desirable to maximize the cooling efficiency and increase the density of cold molecules. Elastic collision involves momentum transfer with no energy changes in internal states. In contrast, inelastic scattering involves changes in rovibrational energy of molecule. If the rate coefficients for inelastic deexcitation collisions with the cold atoms are large, the energy released by the molecules will heat the cold atoms and molecules, and hence lead to trap loss. It is therefore of importance to have some previous knowledge for the behavior of corresponding collisionally elastic and inelastic cross sections under low scattering energy.

The theoretical study on the low temperature behavior of collision cross sections is an active subject recently. There are several investigations of cool collision for different van der Waals systems: He + H_2[7,8], H + H_2[9], He + O2[10], He + CO[11,12], Ar + H_2[13,14], He + F_2[15], He + N_2[16]. These investigations showed that the rovibrational energy transfer can be extremely efficient at very low temperature, and that it is sensitive to the initial rovibrational levels. It was also showed that the inelastic cross sections follow Wigner law and elastic cross sections attain different finite values at very low collision energy, and the resonance structure has its important influence on the quenching rate coefficients.

The studies mentioned above mainly concerned homonuclear diatoms or heteronuclear diatom with weakly angular anisotropy of the potential. Here we extend the study to van der Waals system: Ne + LiH, which contains heteronuclear diatom and presents strong anisotropy of the potential. We investigate the rotational elastic and inelastic cross sections and quenching rate coefficients, examine the limiting behavior at very low collision energy and temperature.

2 Scattering calculation

In our work we implement the close coupling calculation in a Space-fixed frame for rotationally inelastic collision of LiH with Ne. The details are given in our previous work[17]. The cross section for transition from an initial rotational level j to a final level j' can be expressed in terms of the corresponding S matrix elements

$$\sigma_{j\to j'} = \frac{\pi}{(2j+1)k_j^2}\sum_J (2J+1)\times \sum_l\sum_{l'} |\delta_{jj'}\delta_{ll'} - S^J_{jl\to j'l'}|^2 \qquad (1)$$

where J, l and l' are the total, the initial orbital and final orbital angular momentum, respectively. The wave vector for the incoming channel is defined as $k_j = \sqrt{2\mu(E-\epsilon_j)}/\hbar$, where E is total energy, ϵ_j is the initial rotational level and μ is the reduced mass of system. The S matrix can be extracted by matching the solution of multichannel close coupling equation with the asymptotic solution.

The total deexcitation(relaxation) cross section from a given initial state j is given by

$$\sigma_j^{in} = \sum_{j'} \sigma_{j\to j'}(E_j) \tag{2}$$

where the summation excludes purely elastic $j = j'$ transition. The E_j is the kinetic energy in the initial channel, given by $\hbar^2 k_j^2/(2\mu)$. The quenching rate coefficients are calculated by averaging the cross sections over a Boltzmann distribution of the relative kinetic energy at a specified temperature T:

$$r_j(T) = \sqrt{\frac{8}{\pi\mu}}(k_B T)^{-3/2} \times \int_0^\infty dE_j E_j \sigma_j^{in}(E_j) e^{-E_j/k_B T} \tag{3}$$

Here k_B is the Boltzmann constant. In the limit of zero kinetic energy the elastic cross section is finite and is given by[18]

$$\lim_{E_j\to 0}[\sigma_{j\to j}(E_j) = 4\pi(\alpha_j^2 + \beta_j^2] \tag{4}$$

The α_j and β_j relate to the complex scattering length $a_j, a_j = \alpha_j - i\beta_j$, the β_j being proportional to the total inelastic cross section,

$$\beta_j = \lim_{E_j\to 0}\left[\frac{k_j \sigma_j^{in}}{4\pi}\right] \tag{5}$$

or to the zero-temperature quenching rate coefficient

$$r_j = \frac{4\pi\hbar\beta_j}{\mu} \tag{6}$$

3 Results and discussions

We use the PES obtained by Xie and co-workers[19], which is the only version for title system to date. Cross sections for elastic and inelastic scattering are computed for various collision kinetic energies from 10^{-6} up to 300 cm^{-1}. The hybrid modified log-derivative Airy propagator[20] is used to solve the close coupling equation from 0.2 nm to 5 nm. Owing to the large anisotropy of the interaction surface, the rotational basis sets include all the energetically open rotational channels and at least two energetically closed channels at each collision energy. Thirty-two-point Gauss Legendre quadrature is adopted to evaluate the expansion coefficients of potential and the Legendre terms up to $\lambda_{max} = 12$ are included. The results are checked by reasonable changes in propagator step size, maximum distance for the propagation and total number of rotational states included in the basis set.

In Fig. 1 we report the elastic cross section of $j = 0$ extended to very low incident energies. Compared to the previous studies such as for the He − CO[11, 12], H + H_2[9], Ar + H_2[13,14], He − N2[16] systems, this curve presents more complicated oscillational behavior due to the stronger anisotropy of interaction. There exists an unusual very low energy peak around 0.1 cm^{-1} that appears a shape resonance. None of the previous studied systems exhibits a resonance in this energy region. We note a similar peak around 3×10^{-2} cm^{-1} appeared in quenching cross section of He + F_2 ($v = 1$, $j = 0$)[15] system, which is attributed to the contamination of reaction channel there. It isn't likely the case in the title system. The shape resonance is induced by centrifugal barriers related to specific incident orbital angular momentum l. The analyses of partial wave show that the predominant contribution to this resonance comes from partial wave with incident orbital angular state of $l = 2$ for the collisional pair, and the second contribution comes from $l = 1$ state. For Ne-LiH system, there are two local minima on the PES, the deeper one with an equilibrium distance of 0.247 nm at $\theta = 180°$ (corresponding to the linear Ne − LiH) with a well depth of 206.13 cm^{-1}, the shallower one with an equilibrium distance of 0.497 nm at $\theta = 0°$ (corresponding to the linear Ne − HLi) with a well depth of 27.34 cm^{-1} (see Fig. 2 in[20]). This structure of PES of Ne − LiH system is different from that of previous studied systems that possess only one of van de Waals well. If using the classical relation between impact parameter b_l and l: $b_l \sim l/\sqrt{2\mu E}$, we find that $b_{l=1} = 0.29$ nm and $b_{l=2} = 0.58$ nm for $E = 0.1$ cm^{-1}. The former samples short range attractive well and the latter samples long range attractive well. We thus infer this shape resonance may mainly originate from the long range interaction and interpret why this resonance peak can't be seen in the previous studied systems. Indeed, when we exclude the long range interaction from the PES, the resonance character of this peak

becomes ambiguous.

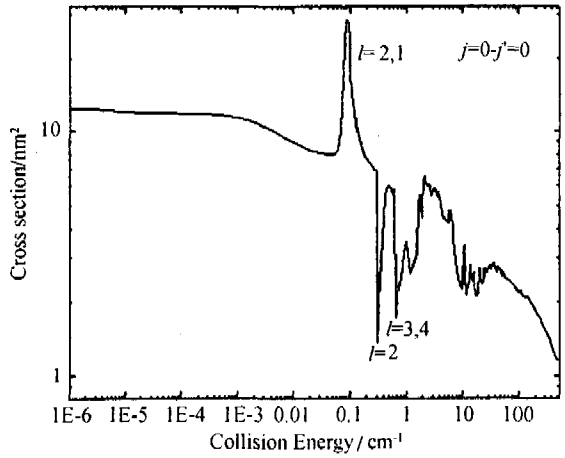

Fig. 1 Elastic cross section of LiH ($j=0$) by collision with Ne as function of the kinetic energy.

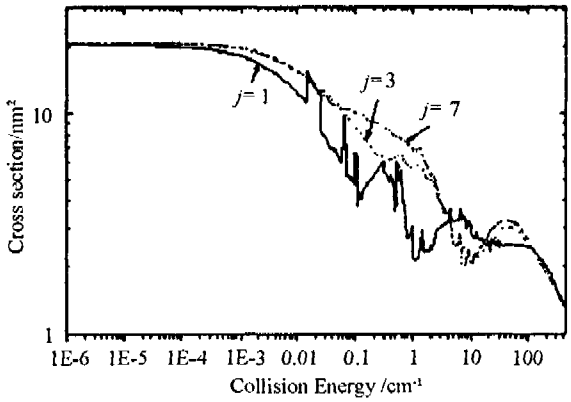

Fig. 2 Elastic cross section of LiH ($j=1,3,7$) by collision with Ne as function of the kinetic energy.

Another interesting feature is that there exist two minima around 0.3 and 0.7 cm^{-1} in Fig. 1. They haven't been found for the mentioned systems. Investigation into the partial wave contribution reveals that the partial waves causing the drastic loss of the elastic cross sections are $l=2$ and $l=3$, 4 respectively. If we multiply the long range part of PES by a factor 0.98 or 1.02, the position and amplitude of two minima change considerable. They are strongly dependent on the precise description of the surface in long range. We then expect a more accurate PES for this system.

It can also be seen there are a series of resonance peaks between 1 and 100 cm^{-1}. In contrast to ^4He-CO[11,12], $He-H_2$[7,8] and $^3He-F_2$[15] system, the resonance structure isn't very sharp. In the present case, no obvious Feshbach resonances are found at least for the rotational levels invested here. The previous studies show that the existence of Feshbach resonance is very sensitive to the details of the interaction potential and dependent to the system investigated. For Ne and LiH collision system, due to deeper well depth and stronger anisotropy of interaction, there are many partial waves contributing to the cross sections. These contributions will suppress the Wigner cusp of s-wave[21] and cause Feshbach resonance ambiguous.

We draw in Fig. 2 the elastic cross sections for $j=1$, 3 and 7. For $j=1$ the curve also displays complicated oscillatory behavior in the energy range $E_j=0.01-100$ cm^{-1} due to the shape resonances, but the position of oscillations is different from that of Fig. 1. When the j increases, the resonance structure decreases. As the collision energy approaches zero three elastic cross sections are very similar to each other and tend to corresponding constant values following Eq. (4) above. The zero energy elastic cross section is about 12.5, 20.5, 21.0, 21.0 nm^2 for $j=0$, 1, 3, 7 respectively.

The total inelastic cross sections for rotational relaxation are shown in Fig. 3 as functions of the collision energies for transitions from $j=1,2,\cdots 7$. In the 0.01 $cm^{-1}\leqslant E_j\leqslant 100$ cm^{-1} region the oscillations exist for all j values. Except $j=3$, the maximum of oscillatory amplitude takes place at about 0.5 cm^{-1}, and increases with j. As energies decrease, the cross section attains its local minimum at about 7×10^{-3} cm^{-1}. At energies below 10^{-4} cm^{-1}, the cross section rises in accord with the Wigner threshold law given by Eq. (5). The energy is small compared to the previous studied systems, where Wigner law's regime applies at energies below 10^{-2} cm^{-1}[10,11,16]. The difference is due to the long range attractive tail of the PES, which enhances contributions from higher partial waves. For $j=1$ the curve deviates from the others because of contribution from leading anisotropy of PES, and the inelastic cross section exceeds the corresponding elastic cross section at energies less than 5×10^{-4} cm^{-1}. The cross sections decrease in general with increasing j except exchanging of $j=3$ and $j=4$. The

detailed analysis reveals that the exchanging mainly originates from stronger coupling of $j=4$ with $j=3$ than that of $j=3$ with $j=2$. When low energy Ne atom approach LiH molecule, the stronger coupling results longer interaction time, which enhances the probability of energy transferring.

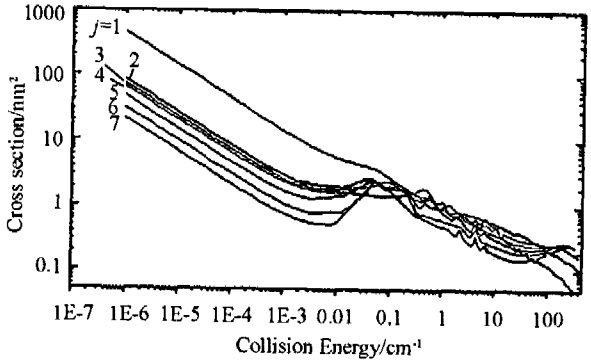

Fig. 3 Total quenching cross sections for initial j from 1 to 7 as function of the kinetic energy.

In Fig. 4 we show the total rotational quenching rate coefficients for different initial j. They all tend to constant values for $T<10^{-4}$ K because the corresponding cross section varies inversely as the velocity. The zero temperature values decrease from 2.9×10^{-11} cm^3 s^{-1} for $j=1$ to 0.14×10^{-11} cm^3 s^{-1} for $j=7$. For $j=7$ there exist a local maximum near 0.1 K and a local minimum near 0.7 K due to the presence of the broader resonance peak as shown in Fig. 3. Similar upturn structure has been seen for other systems in experiment and theoretical studies[11, 22].

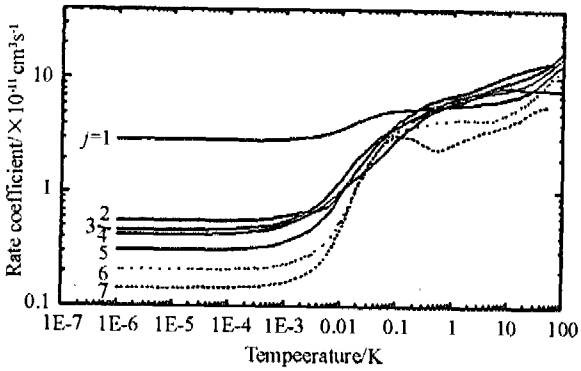

Fig. 4 Rate coefficients for the quenching from $j=1,2,\cdots7$ levels of LiH in collisions with Ne as function of temperature.

In order to characterize quantitatively the dynamics in the limit of vanishing collision energy, we present in Table 1 the values of the real and imaginary parts of the scattering length and the zero temperature rate coefficients. The real parts of the scattering lengths are all positive, suggesting the presence of bound states of the complex system with energies closed to the dissociation threshold of Ne – LiH(j) complex. The large quenching rate coefficients of the order of 10^{-11} cm^{3}s^{-1} attained at zero temperature limiting may cause significant loss in trapping experiments but enhance the possibility of measuring radiation.

Table 1 Scattering length and zero temperature rate coefficients

Initial j state	a_j(nm)	β_j(nm)	$r_j(T\to0)$(cm^{3}s^{-1})
0	1.001	0.000	0.00
1	1.241	0.290	2.9×10^{-11}
2	1.267	0.039	0.55×10^{-11}
3	1.290	0.030	0.42×10^{-11}
4	1.292	0.033	0.47×10^{-11}
5	1.291	0.022	0.31×10^{-11}
6	1.292	0.015	0.20×10^{-11}
7	1.289	0.010	0.14×10^{-11}

4 Conclusions

We have performed detailed quantum mechanical calculation for cold collision of Ne atom with LiH molecule. At incident energies below 10^{-4} cm^{-1}, the elastic cross sections tend to constant limiting values and inelastic cross sections rise in accord with the Wigner threshold law. For a given energy, the total quenching cross sections decrease in general with increasing initial j. In the energy range $E_j=0.01-100$ cm^{-1} the elastic and inelastic cross sections show more complicated oscillational behaviors than other studied systems, due to the stronger anisotropy and two attractive wells on the interaction potential surface. There are one unusual peak and two minima on the $j=0$ elastic cross section, which aren't seen in other systems. The quenching rate coefficients attain their values of the order of 10^{-11} cm^{3}s^{-1} at zero temperature limiting. For $j=7$ the rate coefficient presents upturn structure. It will

be interesting to see if the characters that we predict can be experimentally verified.

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