

## Influence of vibrational excitation on the reaction $\text{Li}(2^2P_j) + \text{H}_2(v=1) \rightarrow \text{LiH}(X^1\Sigma^+) + \text{H}$

Jye-Jong Chen and King-Chuen Lin<sup>a)</sup>

Department of Chemistry, National Taiwan University, Taipei and Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, Republic of China

(Received 4 August 2003; accepted 2 September 2003)

The reaction  $\text{Li}(2^2P_j) + \text{H}_2(v=1) \rightarrow \text{LiH}(X^1\Sigma^+) + \text{H}$  is studied to understand the effect of vibrational excitation on the reaction pathways. The hydrogen molecules in the  $v=1, j=0-3$  levels are populated by using stimulated Raman pumping (SRP). A pump-probe technique is employed simultaneously to initiate the reaction and monitor the products. The pump-SRP and SRP-probe delay time are short enough to allow for the products to be in a nascent state. The population fraction in the  $v=1$  level can be estimated to be 7.5% by using coherent anti-Stokes Raman spectroscopy. As characterized by Boltzmann rotational temperature of 730 K, the rotational state distributions of  $\text{LiH}(v=0)$  obtained with  $\text{H}_2(v=1)$  appear to be unimodal, similar to those obtained with  $\text{H}_2(v=0)$ , but the product yield is enhanced by a factor of 7–8 times. According to the potential energy surfaces calculations, the insertion mechanism in (near)  $C_{2v}$  collision configuration is favored. The  $\text{Li}(2^2P_j) - \text{H}_2$  collision is initially along the  $2A'$  surface in the entrance channel and then transits to the ground  $1A'$  surface, from which the products are formed. When  $\text{H}_2$  stretches to its outer turning point ( $\sim 0.9 \text{ \AA}$ ), the  $2A'$  surface may diabatically couple to the  $1A'$  surface in the attractive region. An energy barrier of  $4300 \text{ cm}^{-1}$  will otherwise obscure the reaction if the  $\text{H}_2$  bond distance is fixed at  $0.75 \text{ \AA}$ . The energy deposited in the  $v=1$  level simply enlarges the  $\text{H}_2$  bond distance to help facilitate the reaction and increase the subsequent product yield. The lack of detection of the product  $\text{LiH}(v \geq 1)$  implies that the exoergic energy by  $2530 \text{ cm}^{-1}$  should not be distributed statistically among different freedom of motions. The vibrational excitation does not seem to open up an additional pathway for the reaction. © 2003 American Institute of Physics.  
[DOI: 10.1063/1.1620997]

Reaction dynamics of electronically excited alkali atoms with the hydrogen molecule has been an attractive topic for study.<sup>1</sup> The reactions between alkali atoms and molecular hydrogen,  $\text{A} + \text{H}_2 \rightarrow \text{AH} + \text{H}$ , are highly endoergic in their ground state, requiring a large deposit of energy to initiate the reaction. In practice it is easily achieved via electronic excitation of the atom. Then, nonadiabatic couplings necessarily occur along the reaction path, from the excited entrance valley to the exit one, as the  $\text{A} + \text{H}_2$  ground state potential surface is adiabatically correlated to the  $\text{AH} + \text{H}$  ground state one. The electronic excitation of the atoms, being usually achieved by using lasers, may open the way to the study of various selective effects such as the influence of potential energy and electronic symmetry, as well as the influence of light polarization and coherence. On the other hand, only limited number of atoms and active electrons are involved in the reaction, allowing for realistic, accurate calculations of potential energy surfaces (PES) and collision dynamics, even in the excited states that are concerned. Therefore, these photochemical reactions offer unique possibilities to detailed, generalized studies of nonadiabatic processes in reaction dynamics.

Among the issues of reaction dynamical complexity hav-

ing been studied, the reaction pathways for  $\text{K},^{2-9} \text{Rb},^{10,11}$  and  $\text{Cs}^{12-20}$  are found to be similar with the following common characteristics: First, these reactions followed a collinear collisional geometry, producing alkali hydrides predominantly via an ion-pair intermediate; however, for the case of Cs, an electron jumping distance was shorter than the harpoon model predicted.<sup>14</sup> Second, the available energy dissipation into vibration of the product, particularly for KH and RbH, generally increased with the principal quantum number. Third, more than 70% of the available energy was released as translation, while only a small fraction was channeled into rotational motion of the alkali hydrides which appeared to be in statistical thermal distributions. The  $\text{Na}(4^2P)$  plus  $\text{H}_2$  reaction is the only exception with a different reaction pathway from K, Rb, and Cs. Kleiber and co-workers<sup>21,22</sup> found that a bimodal rotational distribution of NaH resulted with the minor component peaking at low  $J$  and the major component peaking at high  $J$ . The bimodal nature was thought to stem from a side-on attack along an attractive surface, which determined the microscopic branching late in the exit channel.<sup>21,22</sup> To interpret the insertion preference, Bersohn suggested that the Na atom with a smaller size should suffer from the least repulsion in the insertion approach into the H–H bond.<sup>14</sup>

The scheme,  $\text{Li} + \text{H}_2 \rightarrow \text{LiH} + \text{H}$ , is the simplest chemical reaction after the  $\text{H} + \text{D}_2$  exchange one. The reaction is en-

<sup>a)</sup> Author to whom correspondence should be addressed. Fax: 886-2-23621483; electronic mail: kclin@ccms.ntu.edu.tw

doergic by  $1624\text{ cm}^{-1}$  after excitation of lithium atoms to the  $2p^2P$  state.<sup>23</sup> The  $\text{Li}(2^2P_J) + \text{H}_2$  reaction can start from the first excited potential surface above ground state to yield LiH and H products in their electronic ground states. It necessarily implies nonadiabatic couplings along the reaction path. Up to now, the only available experimental data over the  $\text{Li}(2^2P_J) + \text{H}_2 \rightarrow \text{LiH} + \text{H}$  reaction have been obtained in bulk experiments. For instance, Mysers *et al.* measured the reaction cross section ( $\sigma = 0.10\text{ \AA}^2$ ) using a rate equation model.<sup>24</sup> Lin and co-workers characterized the rotational state distributions of the  $\text{LiH}(X^1\Sigma^+, v=0)$  products to be unimodal with a Boltzmann rotational temperature slightly hotter than the cell itself.<sup>9</sup> It thus suggests a side-on attack of the lithium atom to insert between the two hydrogen ones. Bililign and co-workers also observed the LiH product in the  $\text{Li}(2^2P_J) + \text{H}_2$  reaction to favor a near  $C_{2v}$  collision configuration using far-wing scattering spectroscopy.<sup>25</sup> From a theoretical point of view, Jeung and co-workers predicted that an insertion mechanism be favored, but harpoon mechanism cannot be applied to this system.<sup>23</sup>

In this work, effect of vibrational excitation on the  $\text{Li}(2^2P_J) + \text{H}_2(v=1)$  reaction is studied for the first time. The  $\text{H}_2$   $v=1$ ,  $j=0-3$  levels are populated by using stimulated Raman pumping (SRP). A coherent anti-Stokes Raman spectroscopy (CARS) is employed to determine the population fraction pumped to these levels. With detection of laser-induced fluorescence (LIF), the  $\text{LiH}(X^1\Sigma^+, v=0)$  product yield is found to be greatly enhanced, with rotational state distributions similar to those obtained with the  $\text{H}_2(v=0)$  reaction, under an otherwise identical condition. More insight may be gained into the dynamical complexity from the current reaction.

In the experimental setup, a pump-probe technique applied to heat-pipe oven was similar to the one used previously.<sup>5,6,8,9</sup> The pump beam was a 10 Hz, 5–8 ns pulsed doubled Nd:YAG laser-pumped dye laser, which was used to prepare the Li atom in the  $2p^2P_J$  state at 670.9 nm. The probe dye laser, pumped by another (tripled) Nd:YAG laser, was used to excite the LIF spectra of the LiH product in the  $A^1\Sigma^+ - X^1\Sigma^+$  transition from 360 to 380 nm. The unfocused pump and probe beams, with energies kept less than 100  $\mu\text{J}$  each prior to the reactor propagating opposite to each other, were collimated via an individual pinhole of 0.3  $\text{cm}^2$  cross section. The probe beam was spatially delayed about 10 ns. The zero delay time was defined as the maximum temporal overlap between the pump and probe pulses.

A six-armed heat-pipe oven was used to contain the Li metal, which was heated to  $700 \pm 1\text{ K}$ . The  $\text{H}_2$  gas, regulated at a constant pressure of about 8 Torr monitored by a MKS capacitance pressure gauge, flowed slowly through the reactor. The obtained LIF signal of  $\text{LiH}(X^1\Sigma^+, v=0)$  was transmitted perpendicularly relative to the laser beam through a monochromator and detected by a photomultiplier tube (PMT) enclosed in a cooler at  $-20\text{ }^\circ\text{C}$ . The monochromator functioned as a filter to reduce interference from scattered light. To remain the obtained LiH in a nascent state, a rotational line (6,0) R5 was selected for the measurement of the  $\text{H}_2$ -pressure dependence. Its peak area was linearly proportional to the  $\text{H}_2$  pressure up to 15 Torr at a pump-probe time

delay of 10 ns. The results implied that the rotational cooling and secondary reaction processes were negligible under the conditions adopted throughout the experiments.

A SRP technique was employed to prepare the  $\text{H}_2$  population in the  $v=1$  level. The second harmonic of an Nd:YAG laser at 532 nm was focused into a Raman shifter, filled with 10 atm  $\text{H}_2$  gas, to give out a strong first Stokes and anti-Stokes Raman shift at about 683 and 436 nm, respectively. The output beams at 532 and 683 nm were measured to be 18 and 20 mJ, respectively, prior to the reaction chamber, while the beam at 436 nm was filtered out. Then these two beams were softly focused, with a focal length of 70 cm, and reflected by a dichroic mirror into the center of the reactor, overlapping with the probe beam which was transmitted through the same dichroic mirror. The pump-SRP and SRP-probe delay time were adjusted to be 5 ns each. During such short delay time the prepared  $\text{H}_2$   $v=1$  population could not be relaxed via collisions.<sup>26</sup>

The fraction of population in the  $v=1$  level may be estimated by using CARS. The setup of CARS was composed of two pulsed beams: one from an Nd:YAG laser at 532 nm with 25 mJ and the other from an Nd:YAG laser pumped-dye laser emitting in the range 680–685 nm with 5–6 mJ. With the use of a dichroic mirror ( $M_1$ ), both beams propagating along the same direction are temporarily and spatially overlapped in the center of the reactor. The produced anti-Stokes beam at about 435–437 nm was transmitted through another dichroic mirror ( $M_2$ ) and detected by a PMT positioned at the opposite side of the reactor. While the dye laser was scanned, the CARS rotational spectra of  $\text{H}_2$  ( $v=0, j=0-3$ ) at 700 K may be obtained under the conditions without and with SRP application. The SRP pulses were reflected by the dichroic mirror ( $M_2$ ) and spatially overlapped with the CARS beams impinging from the opposite side of the reactor.

Using the pump-probe technique, Fig. 1 shows a portion of the LIF spectra of LiH (5,0) and (6,0) bands in the  $A^1\Sigma^+ - X^1\Sigma^+$  transition with and without SRP application. The spectral assignments of these rovibrational bands adopt the molecular constants for the X and A states reported by Stwalley and co-workers.<sup>27-29</sup> The obtained spectra are in a nascent state, as examined by the measurements described previously. The rotational intensities obtained with SRP are found to be significantly stronger than those without SRP. However, LiH cannot be detectable with SRP alone, if the pump beam is blocked.

The rotational spectrum in Fig. 1(b) is actually contributed by the reactions with both  $\text{H}_2$   $v=0$  and 1 populations. The fraction of  $v=1$  population with SRP technique may be estimated by using CARS. Figure 2 shows the CARS spectra of four Q-branch transitions of  $\text{H}_2(v=0 \rightarrow 1)$  at 700 K with and without the SRP application. The intensity alternation is caused by the nuclear spin  $I=1/2$  and thus the statistical weights for the even and odd rotational lines are 1 and 3, respectively.<sup>30</sup> The CARS signal is proportional to the square of the population difference between the two Raman transition states of molecule.<sup>31</sup> As shown in Fig. 2(b), a decrease of 28% in populations of all rotational lines of the  $v=0$  level suggests that the  $v=1$ ,  $j=0-3$  levels should be excited si-

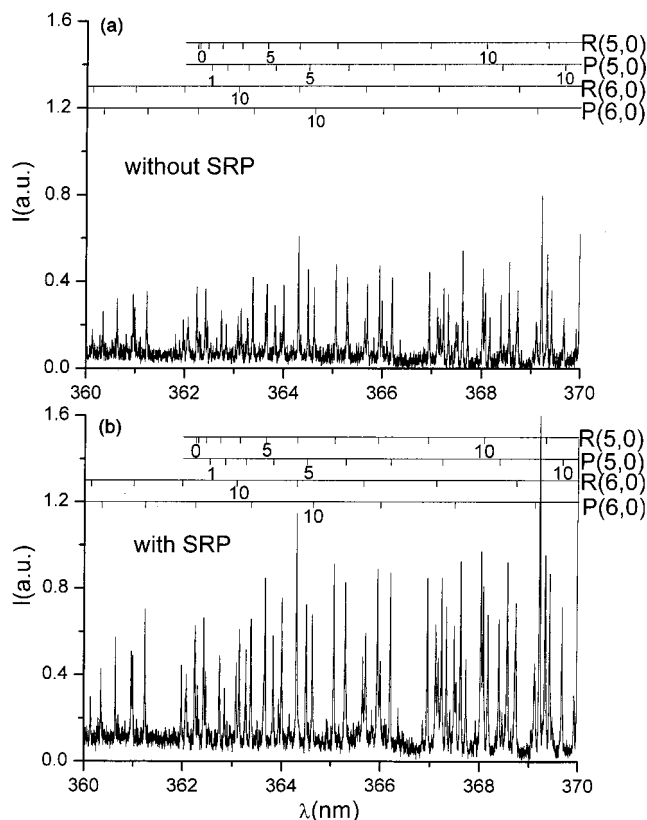


FIG. 1. LIF spectra of  $\text{LiH}(v=0)$  in the  $A^1\Sigma^+ - X^1\Sigma^+$  transition (a) without SRP and (b) with SRP application. The vibrational levels  $v'=5,6$  in the upper state are excited, while the emissions from the (5,5), (6,6) bands are monitored.

multaneously by SRP, different from only a single rovibrational level ( $\text{H}_2 v=1, j=1$ ) prepared in a supersonic jet experiment.<sup>32</sup> The vibrational population is evaluated as a sum of the corresponding rotational peak areas. Accordingly, the population fraction in  $v=1$  pumped by SRP can be estimated to be 7.5% of the total vibrational population in this work. A value more than 30% was previously reported by detection of resonance-enhanced multiphoton ionization (REMPI), under the beam energies of 25 mJ/pulse each for the wavelength at 532 and 683 nm through a 20 cm focal lens into the reaction chamber.<sup>32</sup> The deviation in the beam energy densities and the pressure in the Raman shifter may cause the difference of the SRP efficiency.

By considering the Hönl-London factors, the rotational population distributions of  $\text{LiH}(v=0)$ , as represented by the average intensities of P and R branch lines, are shown in Fig. 3. For the case without SRP [i.e.,  $\text{H}_2(v=0)$ ], the distributions appear to be unimodal, peaking at  $J=4-5$ . The rotational population may be approximately characterized by a statistical thermal distribution, with temperature of  $737 \pm 39$  K estimated from the (6,0) band, in agreement with those reported previously.<sup>9</sup> For the case with SRP, the rotational intensities are contributed by the reactions with 7.5%  $\text{H}_2(v=1)$  and 92.5%  $\text{H}_2(v=0)$ . Accordingly, as shown in Fig. 3, the rotational state distributions of  $\text{LiH}$  for the reaction with  $\text{H}_2(v=1, j=0-3)$  alone may be readily obtained from the rotational spectra given in Figs. 1(a) and 1(b). The Boltzmann rotational temperature is thus determined to be

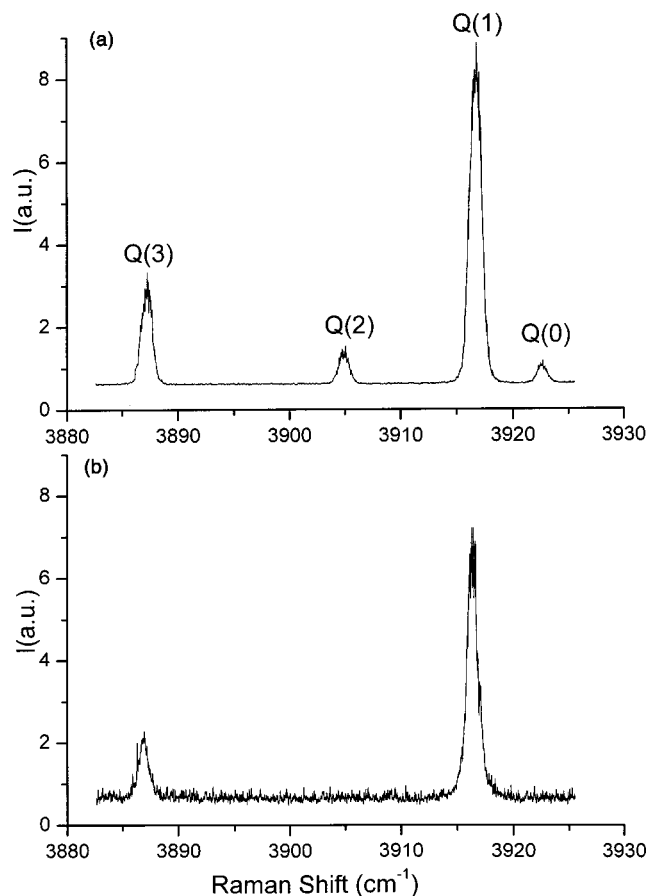


FIG. 2. Rotational spectra of  $\text{H}_2(v=0, j=0-3)$  in the Q-branch transition at a pressure of 8 Torr in a heat-pipe oven at 700 K obtained by using CARS technique under the conditions (a) without SRP and (b) with SRP.

730 K, slightly higher than the oven temperature. While comparing the rotational distributions resulting from the  $\text{H}_2 v=0$  and 1 levels, two aspects may be discerned. First, the product yield and thus the reaction cross section obtained in the  $\text{H}_2(v=1)$  case is enhanced by a factor of 7-8 times. Second, the rotational distributions both appear to be similar to each other. For the case without SRP, the  $\text{LiH } v \geq 1$  popu-

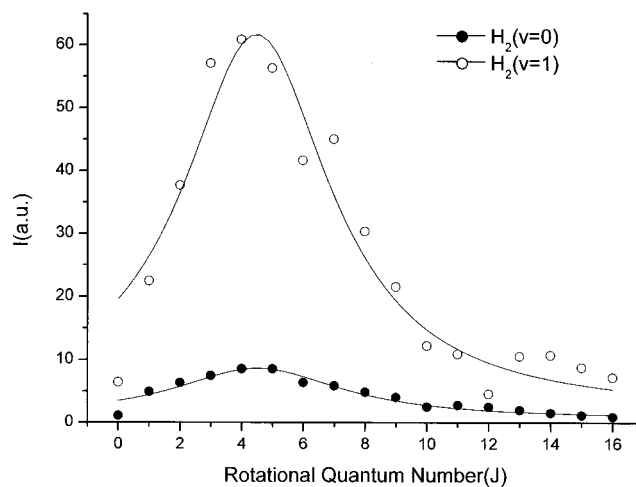


FIG. 3. Rotational population distributions of  $\text{LiH}(v=0)$  determined from the (6,0) band in the reactions with  $\text{H}_2(v=0)$  and  $\text{H}_2(v=1)$ , respectively.

lations were not detectable ( $<0.05 \text{ \AA}^2$ ), since the reaction is endothermic by  $1624 \text{ cm}^{-1}$  calculated by Jeung and co-workers.<sup>23</sup> According to Arrhenius theory, the energy barrier was determined previously to be  $1280 \pm 46 \text{ cm}^{-1}$ , which is probably attributed to such endothermicity.<sup>9</sup> It should be noted that the vibrational excitation of  $\text{H}_2(v=1)$  makes the current reaction become exoergic by  $2530 \text{ cm}^{-1}$ , energetically equivalent to the  $v=2$  level of LiH product. Nevertheless, the population of  $\text{LiH}(v \geq 1)$  has not been detectable either.

According to *ab initio* PES calculations for the  $\text{Li}(2^2P)$  plus  $\text{H}_2(v=0)$  reaction, the reaction pathway favors Li-insertion into the  $\text{H}_2$  bond.<sup>9,23</sup> The colliding species follows a near  $C_{2v}$  coordinate along the  $1B_2$  (or  $2A'$ ) surface and then transits to the lower state from which the products are formed. The curve crossing between the  $1A_1$  and  $1B_2$  surfaces occurs at a barrier about  $4300 \text{ cm}^{-1}$  above the asymptote states of separate reactants with the H–H bond fixed at  $0.75 \text{ \AA}$ . In contrast, the crossing region moves outward to the attractive portion of the  $2A'$  surface, as the  $\text{H}_2$  bond is stretched to  $0.9 \text{ \AA}$ .<sup>9</sup> Therefore, the reaction is feasible to occur as long as  $\text{H}_2$  stretches to its outer turning point.

The vibrational excitation of  $\text{H}_2$  seems to simply enlarge the  $\text{H}_2$  bond distance in the entrance channel to facilitate the reaction and increase the subsequent product yield. The lack of detection of  $\text{LiH}(v \geq 1)$  in the  $\text{Li}(2^2P_j)$  plus  $\text{H}_2(v=1)$  reaction suggests that the excess energy by  $2530 \text{ cm}^{-1}$  should not be distributed statistically among different freedom of motions. The energy deposited in the vibration does not open up an additional reaction channel to make the product distributions otherwise different. The experimental findings confirm the interpretation of reaction pathways based on the PES calculations. Different from the current reaction, the vibrational excitation in the  $\text{O}(^1D)$ ,<sup>33</sup>  $\text{C}(^1D)$ ,<sup>34</sup> and  $\text{O}(^3P)$ ,<sup>35</sup> plus  $\text{H}_2(v=1)$  reactions may change the rotational distributions and thus enhance the probabilities for the reaction pathways which are otherwise negligible in the  $\text{H}_2(v=0)$  reactions.

By analogy with the case of  $\text{Na}(4^2S, 4^2P)$ ,<sup>21,22</sup> the  $\text{Li}(2^2P)$  plus  $\text{H}_2$  reaction favors the insertion mechanism. The small atomic size of Li causes the least repulsion in the insertion approach. An efficient electron back-donation from the metal atom to the antibonding  $\sigma^*$  of the molecular hydrogen may energetically stabilize the  $^2B_2$  (or  $2^2A'$ ) surface. Enlargement of the  $\text{H}_2$  bond distance with vibrational excitation seems to strengthen such stabilization to make the  $^2B_2$  (or  $2^2A'$ ) surface more attractive. Despite the similarity between the reactions of Li and Na involving the  $2A' - 1A'$  nonadiabatic couplings, their resultant rotational state distributions are different. For Li, the rotational distribution in the exit channel may depend on the anisotropy of the  $1A'$  surface. The  $\text{LiH}_2$  collision complex in the minimum energy of the  $1A'$  surface is expected to be in a bent configuration.<sup>9,23</sup> Thus, upon transition to the lower surface, the  $\text{LiH}_2$  collision complex, which decomposes via a bent intermediate, is subject to a weak anisotropic interaction, causing the rotational temperature slightly hotter than the system temperature.

In summary, by using the SRP technique, the effect of vibrational excitation on the dynamical complexity for the

$\text{Li}(2^2P)$  plus  $\text{H}_2$  reaction is investigated. A population fraction of 7.5% pumped to the  $v=1$  level may be estimated with the CARS measurement. The determined rotational state distributions of  $\text{LiH}(v=0)$  with the  $\text{H}_2 v=1$  excitation appear to be similar to those obtained with the  $\text{H}_2 v=0$  reaction, but the product yield (or reaction cross section) is enhanced by a factor of 7–8. According to the PES calculations, the  $\text{Li}(2^2P)$  with  $\text{H}_2 v=0$  and 1 reactions both favor the insertion mechanism. The excess energy in the  $\text{H}_2(v=1)$  case may not randomly flow to the LiH internal states to cause higher levels ( $v \geq 1$ ) populated. The vibrational excitation may not change the effective colliding configuration to open up an additional reaction pathway, but simply enlarges the  $\text{H}_2$  bond distance to facilitate the reaction. The effect of vibrational excitation can be readily interpreted and help understanding of the  $\text{Li}(2^2P)$  plus  $\text{H}_2$  reaction.

This work was supported by the National Science Council, Republic of China, under Contract No. NSC92-2113-M-002-046.

- <sup>1</sup>K. C. Lin and R. Vetter, *Int. Rev. Phys. Chem.* **21**, 357 (2002), and the references therein.
- <sup>2</sup>K. C. Lin and H. C. Chang, *J. Chem. Phys.* **90**, 6151 (1989).
- <sup>3</sup>H. C. Chang, Y. L. Luo, and K. C. Lin, *J. Chem. Phys.* **94**, 3529 (1991).
- <sup>4</sup>Y. L. Luo, K. C. Lin, D. K. Liu, H. J. Liu, and W. T. Luh, *Phys. Rev. A* **46**, 3834 (1992).
- <sup>5</sup>D. K. Liu and K. C. Lin, *J. Chem. Phys.* **105**, 9121 (1996).
- <sup>6</sup>D. K. Liu and K. C. Lin, *J. Chem. Phys.* **107**, 4244 (1997).
- <sup>7</sup>T. H. Wong and P. D. Kleiber, *J. Chem. Phys.* **110**, 6743 (1999).
- <sup>8</sup>Y. C. Hsiao, D. K. Liu, H. S. Fung, and K. C. Lin, *J. Chem. Phys.* **113**, 4613 (2000).
- <sup>9</sup>J. J. Chen, Y. M. Hung, D. K. Liu, H. S. Fung, and K. C. Lin, *J. Chem. Phys.* **114**, 9395 (2001).
- <sup>10</sup>L. H. Fan, J. J. Chen, Y. Y. Lin, and W. T. Luh, *J. Phys. Chem. A* **103**, 1300 (1999).
- <sup>11</sup>M. L. Chen, W. C. Lin, and W. T. Luh, *J. Chem. Phys.* **106**, 5972 (1997).
- <sup>12</sup>C. Crepin, J. L. Picque, G. Rahmat, J. Verges, R. Vetter, F. X. Gadea, M. Pelissier, F. Spiegelmann, and J. P. Malrieu, *Chem. Phys. Lett.* **110**, 395 (1984).
- <sup>13</sup>A. G. Urena and R. Vetter, *Int. Rev. Phys. Chem.* **15**, 375 (1996).
- <sup>14</sup>X. Huang, J. Zhao, G. Xing, X. Wang, and R. Bersohn, *J. Chem. Phys.* **104**, 1338 (1996).
- <sup>15</sup>J.-M. L'Hermite, G. Rahmat, and R. Vetter, *J. Chem. Phys.* **93**, 434 (1990).
- <sup>16</sup>F. X. Gadea, J.-M. L'Hermite, G. Rahmat, and R. Vetter, *Chem. Phys. Lett.* **151**, 183 (1988).
- <sup>17</sup>F. X. Gadea, F. Spiegelmann, M. Pelissier, and J. P. Malrieu, *J. Chem. Phys.* **84**, 4872 (1986).
- <sup>18</sup>J.-M. L'Hermite, *J. Chem. Phys.* **97**, 6215 (1992).
- <sup>19</sup>A. G. Urena and R. Vetter, *J. Chem. Soc., Faraday Trans.* **91**, 389 (1995).
- <sup>20</sup>V. Cavero, J. M. Lmermite, G. Rahmat, and R. Vetter, *J. Chem. Phys.* **110**, 3428 (1999).
- <sup>21</sup>S. Bililign, P. B. Kleiber, W. R. Kearney, and K. M. Sando, *J. Chem. Phys.* **96**, 218 (1992).
- <sup>22</sup>S. Bililign and P. D. Kleiber, *J. Chem. Phys.* **96**, 213 (1992).
- <sup>23</sup>H. S. Lee, Y. S. Lee, and G. H. Jeung, *J. Phys. Chem. A* **103**, 11080 (1999).
- <sup>24</sup>E. G. Mysers, D. E. Murnick, and W. R. Softky, *Appl. Phys. B: Photophys. Laser Chem.* **43**, 247 (1987).
- <sup>25</sup>S. Bililign, B. C. Hattaway, T. L. Robinson, and G. H. Jeung, *J. Chem. Phys.* **114**, 7052 (2001).
- <sup>26</sup>R. L. Farrow and D. W. Chandler, *J. Chem. Phys.* **89**, 1994 (1988).
- <sup>27</sup>W. C. Stwalley and W. T. Zemke, *J. Phys. Chem. Ref. Data* **22**, 87 (1993).
- <sup>28</sup>W. T. Zemke and W. C. Stwalley, *J. Chem. Phys.* **68**, 4619 (1978).
- <sup>29</sup>F. B. Orth and W. C. Stwalley, *J. Mol. Spectrosc.* **76**, 17 (1979).
- <sup>30</sup>G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of*



- Diatomic Molecules* (Van Nostrand Reinhold, Toronto, 1950), pp. 133–139.
- <sup>31</sup>A. C. Eckbreth and P. W. Schreiber, in *Chemical Application of Nonlinear Raman Spectroscopy*, edited by A. B. Harvey (Academic, New York, 1981), p. 27.
- <sup>32</sup>D. A. V. Kliner, D. E. Adelman, and R. N. Zare, *J. Chem. Phys.* **95**, 1648 (1991).
- <sup>33</sup>K. Mikulecky and K.-H. Gericke, *J. Chem. Phys.* **96**, 7490 (1992).
- <sup>34</sup>K. Mikulecky and K.-H. Gericke, *J. Chem. Phys.* **98**, 1244 (1993).
- <sup>35</sup>J. Han, X. Chen, and B. R. Weiner, *Chem. Phys. Lett.* **332**, 243 (2000).