JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 6 8 AUGUST 2003

IR induced *cis*↔*trans* isomerization of 2-naphthol: Catalytic role of hydrogen-bond in the photoinduced isomerization

Takayuki Ebata,[a] Kyouko Kouyama, and Naohiko Mikami
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

(Received 27 May 2003; accepted 11 June 2003)

An infrared laser induced *cis*↔*trans* isomerization has been investigated for 2-naphthol and its hydrogen(H)-bonded cluster with NH_3 in the S_1 electronic state by UV–IR double resonance excitation in a supersonic jet. A specific isomer was pumped to a X–H (X=O, C or N) stretching vibration in S_1 by a sequential UV–IR two-photon excitation, and the resultant product species were analyzed by dispersing their fluorescence. It was found that the IR excitation induces the isomerization for the H-bonded cluster with the excitation less than 3000 cm^{-1}, while no isomerization was found to occur for bare 2NpOH even with an input energy of 3610 cm^{-1}. The substantial reduction of the isomerization barrier height represents evidence of the catalytic nature of H-bonding in the conformational isomerization. It was also found that the isomerization efficiency is very high at low IR frequency and exhibits a marked IR frequency dependence.
[DOI: 10.1063/1.1596831]

The existence and discrimination of the rotational isomers of 2-naphthol (2NpOH) was first demonstrated by Ito and co-workers using electronic spectroscopy combined with a supersonic free jet technique.[1] The rotamers, *cis* and *trans*, originate from the difference in conformation of the OH group with respect to the naphthalene ring. Later, Pratt and co-workers distinguished the two isomers by measuring high resolution electronic spectra.[2] It is reported that the *cis*-isomer is 140 cm^{-1} more stable than the *trans*-isomer in S_0, while in S_1 the *trans*-isomer becomes 180 cm^{-1} more stable than the *cis*-isomer.[3] Though the barrier height of the isomerization along the torsional coordinate of the OH group in 2NpOH has not been reported in either state, it is thought to be very similar to that of phenol, 1200 cm^{-1} in S_0,[4] and 4710 cm^{-1} in S_1, respectively.[5] The dynamics and mechanism of the conformational isomerization has recently been paid much attention because of the fundamental importance in chemistry, as well as in biochemistry, especially for understanding the three dimensional structure of flexible biorelevant molecules.[6]

In this Communication, we report a study on laser assisted *cis*↔*trans* isomerization of 2NpOH and its hydrogen(H)-bonded cluster with NH_3 in S_1 by using UV–IR double resonance spectroscopy. A specific isomer or its cluster in a jet is pumped to a X–H stretching vibration in S_1 by a sequential UV–IR two-photon excitation, where X refers to O, C, or N atom. The isomerization will occur when the X–H stretching energy flows into the torsional vibration of the OH group, exceeding the barrier height of the isomerization. We investigated the process putting our emphasis on the following issues: The first is whether *cis*↔*trans* isomerization actually occurs in the energy region examined in the present work. The second is whether this reaction exhibits any selectivity. In such a case, what is a major factor for the selectivity? The third is how the barrier height and the dynamics of the isomerization are affected by H-bonding to the OH group. We will verify those issues under a challenging attempt for the laser control of the isomerization.

The experimental setup of UV–IR double resonance spectroscopy has been described in our previous papers.[7–9] Jet-cooled 2NpOH and its cluster with NH_3 were produced by the supersonic expansion of $2NpOH/NH_3$ gaseous mixture, seeded in helium carrier gas. A specific species in the jet was pumped to the zero-point level in S_1 with a UV light, followed by an IR excitation to the X–H stretching vibration. The vibrationally-excited molecules or clusters in S_1 will immediately relax by intramolecular or intracluster vibrational energy redistribution (IVR) and emit broad fluorescence in the wide frequency region. If isomerization occurs, the generated isomer emits fluorescence in different frequency region from the initial species because each isomer has own electronic transition frequency. Thus we can discriminate IVR or isomerization by dispersing the emission by using a monochromator. The X–H stretching energies are, in general, larger than the H-bonding energy, and the vibrationally excited clusters may predissociate and generate 2NpOH fragments in S_1. Since most of the input energy is consumed for the dissociation of the H-bond, the generated 2NpOH will be internally cool and emit sharp fluorescence in the band origin region, which can also be discriminated. The IR spectra of 2NpOH and its cluster in S_1 are obtained by scanning the IR frequency while monitoring either the emission from the IVR generated levels[9] or the photofragment emission.[8]

The UV light was a second harmonic of Nd:YAG laser pumped dye laser. Tunable IR laser light in the 3 μm region was obtained by difference frequency generation between the second harmonic of another Nd:YAG laser and the Nd:YAG laser pumped dye laser output by using a $LiNbO_3$ crystal. The delay time between the UV and IR pulses was set to ten

---

[a] Electronic mail: ebata@qclhp.chem.tohoku.ac.jp

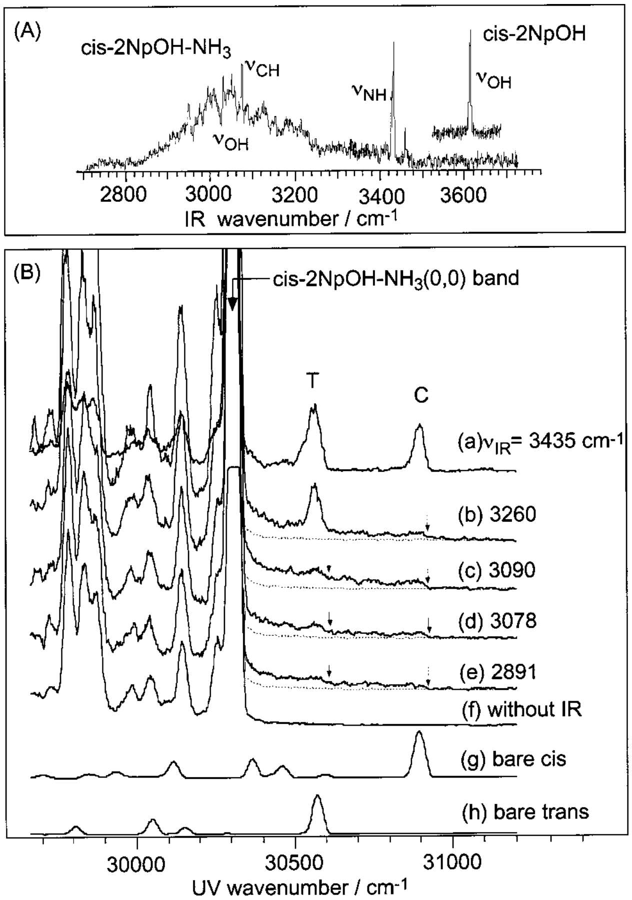

FIG. 1. (A) IR spectra of bare *cis*-2NpOH and *cis*-2-NpOH-NH_3 in the S_1 state. (B) (a)–(e) Dispersed fluorescence (DF) spectra of *cis*-2-NpOH-NH_3 obtained by UV–IR excitation with various IR frequencies. The UV frequency is fixed to the 0,0 band. The arrows indicate the position of steps. See the text. (f) DF spectrum of *cis*-2-NpOH-NH_3 from the zero-point level without the IR light. This spectrum is overlaid on the spectra (a)–(e). (g), (h) DF spectra of bare *cis*-2NpOH and *trans*-2NpOH from their zero-point levels.

nanoseconds. The laser beams were coaxially introduced into a vacuum chamber, crossing the free jet. An $f=250$ mm monochromator was used to disperse the fluorescence. Typical slit width was 100 μm.

The electronic transitions of 2NpOH and its H-bonded clusters have been reported by several groups.[1,10–13] The band origin of *cis*- and *trans*-isomer of bare 2NpOH is located at 30 903 and 30 585 cm^{-1}, respectively, and that of the 1:1 H-bonded cluster with NH_3 is located at 30 318 and 29 964 cm^{-1}, respectively. Figure 1(A) shows the IR spectra of bare *cis*-2NpOH and *cis*-2NpOH-NH_3 in S_1, which were obtained by fixing the UV frequencies to the band origins of each species and monitoring either the relaxed or the fragment emission. The OH stretch of bare *cis*-2NpOH appears at 3609 cm^{-1}. In *cis*-2NpOH-NH_3, we see two sharp peaks at 3400–3500 cm^{-1} and a broadband at 2800–3300 cm^{-1} with its center frequency at 3050 cm^{-1}. From a comparison of the IR spectrum in S_1 with the reported spectrum in S_0,[13] we assign the sharp bands to the NH stretching vibrations of NH_3, and the broadband to the H-bonded OH stretching vibration of 2NpOH. A large reduction of the OH stretch frequency (560 cm^{-1}) is due to a strong H-bonding between 2NpOH in S_1 (Ref. 14) and a strong base, NH_3.

We examined the IR laser induced isomerization for both bare 2NpOH and 2NpOH-NH_3 in S_1. As a result, we found that the isomerization occurs only in the cluster but not in the bare molecule in the examined energy region of 2900–3610 cm^{-1}. We first present the result of 2NpOH-NH_3 and then discuss the result of bare molecule. Since the IR spectrum of 2NpOH-NH_3 is extremely broad as seen in Fig. 1(A), we were able to pump the cluster to various energies by tuning the IR laser frequency along the broad IR band. In Fig. 1(B), traces (a)–(e) represent the dispersed fluorescence (DF) spectra of *cis*-2NpOH-NH_3 observed after the UV–IR excitation with various IR frequencies, being compared with the DF spectrum obtained without IR excitation, trace (f). In the DF spectra with low IR frequency excitations, traces (c)–(e), a broad emission is seen at 30 300–30 920 cm^{-1}. The broadness indicates that the emitting species is internally very hot, so that we assign the broad emission as the fluorescence from the levels generated by IVR of the cluster. In the broad emission spectrum, traces (c)–(e), we notice that there is a step-like feature at 30 920 and 30 600 cm^{-1}, which are marked by arrows. We will discuss the step-structure later. In the DF spectrum with 3260 cm^{-1} excitation, trace (b), a sharp band (band T) emerges at 30 580 cm^{-1}, which is overlapped with the broad emission having a step at 30 920 cm^{-1}. In the case of the 3435 cm^{-1} excitation, trace (a), another sharp band (band C) emerges at 30 900 cm^{-1}. It should be noticed that the broad emission is not seen in trace (a).

The new bands T and C, are undoubtedly assigned to the band origins of bare *trans*- and *cis*-2NpOH, respectively, by the comparison with the S_1-S_0 excitation spectrum. Actually, the DF spectra of bare *cis*- and *trans*-2NpOH from their band origins, traces (g) and (h), clearly show a good coincidence of the bands T and C to the band origins of *trans*- and *cis*-2NpOH, respectively. Thus, we conclude that these species are generated by predissociation of the vibrationally excited *cis*-2NpOH-NH_3 in S_1. The important point from this observation is that the *trans*-2NpOH fragment is generated from *cis*-2NpOH-NH_3, that is, *the cis→trans isomerization is occurring in cis-2NpOH-*NH_3. Furthermore, in the 3260 cm^{-1} excitation, only the *trans*-2NpOH fragment is generated as seen in trace (b), indicating that the isomerization proceeds with almost 100% efficiency at this energy.

In order to make these characteristics clear, we observed relative yields of the two fragments as a function of the IR frequency. Figure 2(a) shows the *trans*-2NpOH fragment yield spectrum by the UV–IR excitation of *cis*-2NpOH-NH_3, representing that the appearance energy of the *trans*-2NpOH fragment from 2NpOH-NH_3 is 3090 (±10) cm^{-1}. We carried out similar measurement for the *cis*-2NpOH fragment. However, the IR absorption intensity was weak at the appearance energy of this fragment and we could not obtain *cis*-2NpOH yield spectrum with a good S/N ratio. Instead, we determined the appearance energy of the *cis*-2NpOH fragment by measuring the relative ratio of the two fragments as a function of the IR frequency as shown in Figs. 2(b) and 2(c). From Fig. 2(c), the appearance energy of the *cis*-2NpOH fragment was determined to be 3280 (±10) cm^{-1}.

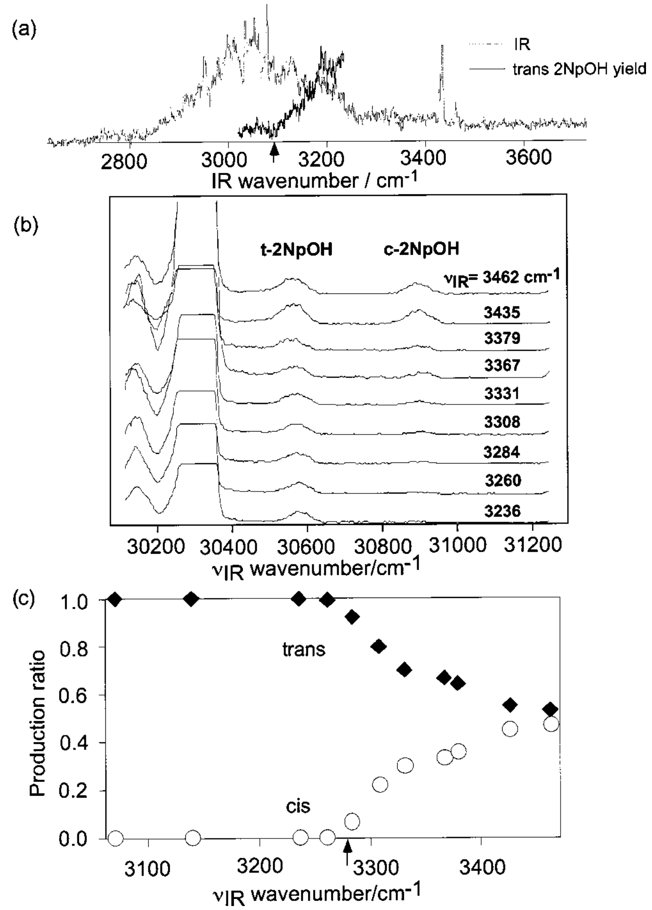

FIG. 2. (a) IR spectrum of *cis*-2NpOH-NH_3, and *trans*-2NpOH photofragment yield spectrum from *cis*-2NpOH-NH_3 in S_1. The arrow indicates the appearance energy (3090 cm^{-1}) of *trans*-2NpOH. (b) DF spectra of *cis*-2NpOH-NH_3 obtained by the UV–IR excitation with various IR frequencies. The spectra are normalized to the fluorescence intensity of *trans*-2NpOH photofragment. (c) Ratio of *cis/trans* 2NpOH photofragment yields vs the IR frequency. The arrow indicates the appearance energy (3280 cm^{-1}) of *cis*-2NpOH fragment.

As mentioned above, we found that the IR induced isomerization does not occur for bare 2NpOH in the examined energy region of 3000–3609 cm^{-1}. The high energy limit, 3609 cm^{-1}, is the OH stretch vibrational frequency of bare 2NpOH, the highest frequency fundamental. The DF spectrum after the IR excitation showed only a broad feature due to IVR of the excited species but emission attributable to the isomerized species was not observed. Therefore, the isomerization barrier height of bare 2NpOH in S_1 is larger than 3609 cm^{-1}. The actual barrier height is thought to be larger than this energy because in phenol, having a similar geometrical and electronic structure with 2NpOH, the barrier height of the torsional motion of the OH group is reported to be 4710 cm^{-1} in S_1.[5] Since the isomerization occurs at 3090 cm^{-1} in *cis*-2NpOH-NH_3, we conclude that the barrier height is substantially reduced upon the H-bonding with NH_3. That is, *the H-bonded NH_3 is acting as a catalyst of the conformational isomerization.*

Though it would be difficult to specify the reason for the substantial reduction of the barrier height upon the H-bonding, we can predict two origins: one is the fact that 2NpOH turns to be a strong acid in S_1. It is known that the acidity of 2NpOH drastically increases from S_0 ($pKa=9.8$) to S_1 ($pKa=2.4$),[14] leading to the excited state proton transfer (ESPT) reaction in condensed phase. Though the ESPT reaction is not reported in the 1:1 cluster, it is quite possible that the OH bond is largely lengthened in the H-bonded cluster in S_1. As the O–H bond stretches, the Coulombic contribution to the H-bonding will increase in the cluster, which may lead to a loss of the bond directionality and a reduction of the barrier height along the torsional coordinate of the OH group. The other origin is the interaction of the nearby $\pi\sigma^*$ state. The importance of this state on the photochemistry of aromatic hydrocarbons has been recently proposed by Sobolewski *et al.*[15–17] This state is predicted to be located nearby S_1 and may cause the excited state hydrogen transfer reaction (ESHT) in the clusters.[18,19] In case of aniline, in fact, we have experimentally proved the existence of this state.[9] A theoretical support is highly demanded for the information of the transition state structure and the barrier height.

So far, we did not discuss the possibility of the isomerization below the H-bond dissociation energy. It will be very important to reveal whether the isomerization is accompanied with the H-bond dissociation. As we mentioned before, we found step-like features at 30 920 and 30 600 cm^{-1} in the DF spectra when the IR excitation energy was lower than the dissociation limit. The difference 320 cm^{-1} between the two steps is very close to the difference of the electronic transition frequencies of the *cis*- and *trans*-2NpOH-NH_3 clusters. Thus, the steps at 30 920 and 30 600 cm^{-1} are thought to be high frequency limits of the emission from the redistributed levels of *cis*- and *trans*-2NpOH-NH_3, respectively, generated by IVR and/or isomerization of the IR excited *cis*-2NpOH-NH_3. Therefore, we conclude that the isomerization occurs without accompanying the H-bond dissociation, and the upper limit of the isomerization barrier height is determined to be 2891 cm^{-1}.

Another noticeable feature is that the production efficiency of the isomerized fragment is very high at low IR excitation energy region. As was described before, we obtained the threshold energies of the productions of *trans*- and *cis*-2NpOH fragments from *cis*-2NpOH-NH_3 to be 3090 and 3280 cm^{-1}, respectively. This means that only the *trans*-2NpOH fragment is produced from *cis*-2NpOH-NH_3 at 3090–3280 cm^{-1}. This high selectivity at the low IR frequency excitation can be explained from heat of formation of each species. Figure 3 shows the energy diagram of 2NpOH and 2NpOH-NH_3 in S_0 and S_1. The H-bond energy of *cis*-2NpOH-NH_3 in S_1 can be set to 3280 cm^{-1} from the appearance energy of *cis*-2NpOH fragment as shown in Fig. 2(c). Accordingly, the binding energy in S_0 is obtained to be 2695 (±10) cm^{-1} from the binding energies in S_1 and electronic transition frequencies of bare *cis*-2NpOH and *cis*-2NpOH-NH_3. By assuming the H-bond energy is the same between the *cis*- and the *trans*-forms in S_0, we obtain the H-bond energy of *trans*-2NpOH-NH_3 in S_1 to be 3316 (±10) cm^{-1}, from the S_1-S_0 transition frequencies. It should be mentioned that the obtained H-bonding energy for 2NpOH-NH_3 in S_0 is in good agreement with that of 1NpOH-NH_3 (2680 cm^{-1}) reported by Bürgi *et al.*[20]

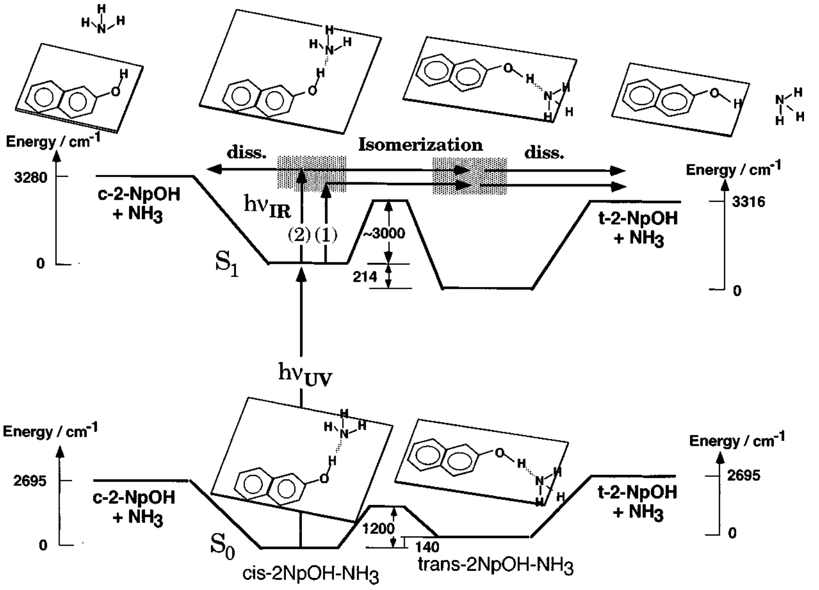

FIG. 3. Energy diagram of the *cis*- and *trans*-2NpOH-NH_3 clusters in S_0 and S_1. Two reaction schemes, (1) and (2), starting from the *cis*-2NpOH-NH_3 cluster are shown: Scheme (1) corresponds to the case with the IR energy lower than the "*cis*-2NpOH+NH_3" dissociation limit. Scheme (2) corresponds to the IR excitation above the "*cis*-2NpOH+NH_3" dissociation limit.

Based on the energy levels in Fig. 3, we discuss the competitive channels for the isomerization and the dissociation. In S_1 of 2NpOH-NH_3, *trans*-isomer is 214 cm^{-1} more stable than that of *cis*-isomer. When the *cis*-2NpOH-NH_3 cluster is excited to the vibrational levels below 3280 cm^{-1} (case 1 in Fig. 3), the energy is not large enough to break the H-bond in the *cis*-form. However, if the *cis*-form cluster isomerizes to the *trans*-form, it can dissociate into *trans*-2NpOH (in S_1) and NH_3, because the total energy of 3494 (=214+3280) cm^{-1} is higher than the dissociation energy of *trans*-2NpOH-NH_3. Thus, only the *cis*→*trans* isomerization/dissociation channel is possible at 3090–3280 cm^{-1}. On the contrary, when *cis*-2NpOH-NH_3 is excited above 3280 cm^{-1} (case 2), the dissociation channel of the *cis*-2NpOH-NH_3 becomes open and the two channels will compete, and we will observe the emission of both the *cis*- and *trans*-2NpOH fragments. To verify the energy constraint reaction mechanism, we carried out the similar study for the *trans*-2NpOH-NH_3 cluster. In the examined IR frequency region of 3330–3435 cm^{-1}, we identified only the *trans*-2NpOH production channel, which is in good agreement with the energy diagram of Fig. 3. Even the highest energy of 3435 cm^{-1} is 59 cm^{-1} lower than the *cis*-2NpOH production channel. The experiment for higher IR excitation could not be performed because of the weak absorption of *trans*-2NpOH-NH_3 compared to that of *cis*-2NpOH-NH_3.

In conclusion, IR laser assisted *cis*–*trans* isomerization has been applied to the H-bonded cluster of 2NpOH in S_1, using UV–IR double resonance spectroscopic method. We found that the H-bonding to the OH group substantially reduces barrier height of the conformational isomerization. The isomerization starting from the *cis*-form H-bonded cluster showed a characteristic energy dependence. At low internal energies the *cis*→*trans* isomerization followed by the H-bond dissociation is dominant, resulting in the high yield of the isomerized phtotofragment. With the energy increases, the predissociation channel within the *cis*-form cluster competes with the isomerization. Further studies on other clusters with wider energy range are now in progress for the detailed understanding of the dynamics of the isomerization and the predissociation.

The authors wish to thank Professor Christophe Jouvet, Professor Claude Dedondor Lardeux, and Professor David Pratt for their helpful discussions and suggestions.

[1] A. Oikawa, H. Abe, N. Mikami, and M. Ito, J. Phys. Chem. **88**, 5180 (1984).
[2] J. R. Johnson, K. D. Jordan, D. F. Plusquellic, and D. W. Pratt, J. Chem. Phys. **93**, 2258 (1990).
[3] J. M. Hollas and M. Z. bin Hussein, J. Mol. Spectrosc. **127**, 497 (1988).
[4] K. Kim and K. D. Jordan, Chem. Phys. Lett. **218**, 261 (1994).
[5] G. Berden and W. L. Meerts, J. Chem. Phys. **104**, 972 (1996).
[6] B. C. Dian, A. Longarte, and T. S. Zwier, Science **296**, 2369 (2002).
[7] T. Ebata, A. Fujii, and N. Mikami, Int. Rev. Phys. Chem. **17**, 331 (1998).
[8] Y. Matsumoto, T. Ebata, and N. Mikami, J. Phys. Chem. A **105**, 5727 (2001).
[9] T. Ebata, C. Minejima, and N. Mikami, J. Phys. Chem. A **106**, 11070 (2002).
[10] T. Droz, R. Knochenmuss, and S. Leutwyler, J. Chem. Phys. **93**, 4520 (1990).
[11] M. Schutz, T. Bürgi, and S. Leutwyler, J. Chem. Phys. **99**, 1469 (1993).
[12] D. F. Plusquellic, X.-Q. Tan, and D. W. Pratt, J. Chem. Phys. **96**, 8026 (1992).
[13] Y. Matsumoto, T. Ebata, and N. Mikami, J. Mol. Struct. **552**, 257 (2000).
[14] A. Weller, Prog. React. Kinet. **5**, 273 (1970).
[15] A. L. Sobolewski and W. Domcke, Chem. Phys. Lett. **329**, 130 (2000).
[16] A. L. Sobolewski and W. Domcke, J. Phys. Chem. A **105**, 9275 (2001).
[17] A. L. Sobolewski, W. Domcke, C. Dedonder-Lardeux, and C. Jouvet, Phys. Chem. Chem. Phys. **4**, 1093 (2002).
[18] G. A. Pino, C. Dedonder-Lardeux, G. Grégoire, C. Jouvet, S. Martrenchard, and D. Solgadi, J. Chem. Phys. **111**, 10747 (1999).
[19] S. Ishiuchi, K. Daigoku, M. Saeki, M. Sakai, K. Hashimoto, and M. Fujii, J. Chem. Phys. **117**, 7077 (2002).
[20] T. Bürgi, T. Droz, and S. Leutwyler, Chem. Phys. Lett. **246**, 291 (1995).