Determination of the Intermolecular potential energy surface of Ar-NO
(Ar-NO の分子間相互作用ポテンシャルの決定)

Graduate School of Arts and Sciences, The University of Tokyo
Yoshihiro Sumiyoshi and Yasuki Endo

I. Introduction

High-resolution spectroscopy of an open-shell complex, Ar-NO, in the electronic ground state has been performed by Mills ,[1] where the fine and hyperfine structures were clearly resolved. The most stable configuration of Ar-NO has thus been confirmed to be T-shaped. They have performed a least-squares analysis using an effective Hamiltonian for a doublet asymmetric-top, considering the hyperfine interaction for the N nucleus and the Renner-Teller effect due to the coupling between the angular momentum of the unpaired electron and the internal motion. However, the observed data were not able to be reproduced within the experimental accuracy, where the standard deviation of the fit was 6,700 kHz. The failure of the fitting was ascribed to a large amplitude zero-point vibration. In the present study we have made a progress for this problem. All the reported data by Mills . could be reproduced almost within the experimental accuracy by employing the analysis using a free-rotor model developed in our recent studies for open-shell complexes, Ar-OH and Ar-SH.[2-4] A 2-dimensional intermolecular potential energy surface (2D-IPS) for Ar-NO has been determined from the analysis. Furthermore, based on the determined 2D-IPS, additional pure rotational (-type) and ro-vibrational (-type) transitions were observed by Fourier-transform microwave spectroscopy, where the transition frequencies were predicted within 1 MHz from the observed using the determined 2D-IPS. This result indicates that the 2D-IPS is accurate at least near the minimum point.

II. The determined 2D-IPS of Ar-NO

The method of the analysis using the free-rotor model is almost the same as that used in our previous studies in Refs. 2–4. The 2D-IPS consists of two adiabatic potential energy surfaces, depending on whether the unpaired electron orbital of the NO monomer is parallel (') or perpendicular ('') to the molecular plane when $\theta \neq 0^\circ$, where the Ar…NO configuration corresponds to $\theta = 0^\circ$ in terms of the Jacobi coordinate system. The potential term is re-expressed by taking the sum, $(\;_{'} + \;_{''})/2$, as the average potential, $_{\Pi}(\;, \theta)$, and the difference, $(\;_{'} - \;_{''})/2$, as the difference potential, $_2(\;, \theta)$, from the two adiabatic potential surfaces. $_{\Pi}(\;, \theta)$ is parameterized by adopting the Maitland-Smith form,

$$_{\Pi}(\;, \theta) = \sum \varepsilon \quad (\cos\theta) \left[\frac{6\;(\;, \theta)^{(\;,\theta)} - (\;, \theta) \cdot (\;, \theta)^{6}}{(\;, \theta) - 6} \right],$$

where $(\;, \theta) = \sum \quad (\cos\theta) / \quad$, $(\;, \theta) = \sum \quad (\cos\theta) + \gamma \left[1/ \;(\;, \theta) - 1 \right]$ and is the Legendre functions. $_{2}(\;, \theta)$ is assumed to have a following functional form,

$$_{2}(\;, \theta) = \left[\sum_{=2}^{5} \;_{2} \quad _{2}(\theta, 0) \right] \exp\left\{ -\left[\beta + \alpha \;\, ^{2}_{2}(\theta, 0) \right] (\quad - \quad) \right\} - \frac{\kappa \;\, ^{2}_{2}(\theta, 0)}{6}.$$

The fitted potential parameters are listed in the upper panel of the table along with those determined by calculations at the RCCSD(T)/aug-cc-pVTZ+bf level of theory, which are used as the initial values for the least-squares fitting. Owing to a large number of data, including pure rotational transitions in different bending vibrational states and ro-vibrational transitions, the intermolecular distance and its angular dependence, , have been determined precisely.

Table. Potential parameters[a]

	Fitted	
ε_1 /cm^{-1}	-3.05 (11)	-4.6199
^{0} /Å	3.8117 (13)	3.8341
^{1} /Å	0.0784 (38)	0.1202
^{2} /Å	0.4096 (30)	0.3839
^{3} /Å	0.105 (11)	-0.0142
$^{2}_{2}$ /cm^{-1}	-14.23 (31)	-11.6282
$^{3}_{2}$ /cm^{-1}	-12.52 (40)	-10.6730
$^{4}_{2}$ /cm^{-1}	-23.38 (53)	-18.8931
β/ Å	2.348 (70)	3.2125
	Fitted	NO
γ / cm^{-1}	0.487 (60)	0.006611
/ cm^{-1}	0.01036 (27)	0.01169
$_{2}$ / MHz	93.081 (67)	92.66
/ MHz	44.0(2.4)	41.79
/ MHz	112.520 (47)	112.60
$_{1}$ / MHz	-4.79 (36)	-1.841
$_{2}$ / MHz	-38.2 (5.7)	-24.23
σ_{fit} /kHz	40	

[a] The numbers in parentheses are 1 σ

In the analysis, most of the molecular parameters of the NO monomer were optimized as shown in the lower panel of the table. Although many of the parameters are almost unchanged from the monomer values, the spin-rotation constant, γ, and the quadrupole coupling constants are changed much to reproduce the observed frequencies within the experimental accuracy, which possibly indicates certain induced effect to the unpaired electron in the NO monomer upon the complex formation. Details of the analysis and the determined 2D-IPS will be given in the talk.

References

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