

## Collision-induced absorption spectra of CsXe system studied by SAC-CI theory

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Collision-induced absorption spectra of the Cs–Xe system is studied theoretically by SAC-CI (symmetry adapted cluster configuration-interaction) theory. The origin of the 6S–5D dipole-induced transition is the existence of 5d  $\Sigma$  and 5d  $\Pi$  quasi-molecular states. The quasistatic model is used for calculations of reduced absorption coefficients. The calculated profiles of the collision-induced absorption spectra reproduce well the experimental spectra.

The optical s–s and s–d transitions of alkali atoms are dipole forbidden. However, when noble gas is admitted into alkali vapour, collisional interaction between alkali atoms and noble gas makes these transitions dipole allowed and a new absorption band is observed near the position of the originally forbidden line [1–4]. This phenomenon is called collision-induced absorption. The position and the profile of the collision-induced absorption sensitively reflect interatomic potentials of the ground and excited states of the alkali–noble gas system and the (induced) transition moments between them. We are interested in this aspect of the collision-induced absorption. Moe et al. [1] reported detailed absorption spectra for the Cs–noble gas and Rb–noble gas systems.

Elucidations of the mechanisms and theoretical evaluations of the line profiles have been carried out by several workers [5–11]<sup>#1</sup>. For the Cs–Xe system, Gallagher and Holstein [6] investigated the line-core region by a perturbative method. Pascale and Vandeplanque [8] calculated adiabatic potential energy curves of alkali–noble gas systems using a semi-empirical model of Baylis [9] and investigated the wing region. Oscillator strengths for the induced dipole transitions were also reported by Pascale [10]. However, their calculated spectra are somewhat dif-

ferent from the experimental ones for the Cs–Xe system [11].

In this paper, we study the collision-induced absorptions of the Cs–Xe system by an ab initio method including electron correlations. This system shows relatively strong interactions and its spectra represent most of the features common to the alkali–noble gas systems [1]. We are interested in the Cs–Xe interactions in a relatively shorter ( $R_{\text{Cs-Xe}} < 10 \text{ \AA}$ ), i.e., the so-called wing region, where van der Waals interactions, overlap interactions and repulsive interactions cooperatively determine the interatomic potentials. We do not study very long-range ( $R_{\text{Cs-Xe}} > 10 \text{ \AA}$ ) interactions, which are reflected in the line-core region of the spectra. Since the spectral profiles depend sensitively on the potential energy curves of the ground and excited states and on the induced transition dipole moments between them, we need a theory which is able to describe both ground and excited states to a considerable accuracy.

As such a theory, we use SAC (symmetry adapted cluster) [12] and SAC-CI [13] theories. The details and the reliability of the SAC/SAC-CI method have been reported elsewhere [12–16]. The basis set we use is fairly flexible. The relativistic effective-core potential [17] is used for the cores of both the Cs and Xe atoms. The outermost nine and eight electrons of the Cs and Xe atoms, respectively, are explicitly treated. The Cs basis consists of the (12s5p)/

<sup>#1</sup> For review articles, see ref. [5].

[3s4p] set of Wadt and Hay [17] augmented with a primitive (6s1p) set taken from Langhoff et al. [18] and three d functions whose exponents are the same as those of the outer three primitives of the [4p] set. The Xe basis set is (3s3p)/[1s2p] [17] augmented with the primitives (3s2p) of Ermler et al. [19] and the (2d) set of Huzinaga [20]. The final set is written as [8s5p3d] for Cs and [4s4p2d] for Xe. We select all of the 8 occupied valence orbitals ( $5s_{Xe}5p_{Xe}5s_{Cs}5p_{Cs}6s_{Cs}$ ) and the lower 41 unoccupied orbitals as an active space. In the SAC-CI step, we do not do configuration selection for linked terms and the resultant dimensions of SAC-CI are 3961 ( $\Sigma$  states), 3370 ( $\Pi$  states) and 2788 ( $\Delta$  state) for all the nuclear separations. Calculations are carried out at the Cs–Xe distances of 3.0, 3.5, 3.75, 4.0, 4.25, 4.5, 4.7, 5.0, 5.25, 5.5, 5.75, 6.0, 6.5, 7.0 and 10.0 Å. The SCF orbitals are calculated with the program GAMESS [21] and the SAC/SAC-CI calculations are performed by the program SAC85 [22]. In the quasistatic model [6,23–25], the reduced absorption coefficients are given by

$$\frac{k(\lambda)}{n_G n_A} = \sum_{R_c} \frac{4\pi^3}{3\lambda} |D(R_c)|^2 \times \left( \frac{4\pi R_c^2}{|d[V_e(R) - V_g(R)]/dR|_{R_c}} \right) \times \exp\left(-\frac{V_g(R_c) - V_g(\infty)}{k_B T}\right),$$

where  $n_G$  and  $n_A$  are the density of the perturber Xe and the absorber Cs,  $D(R)$  the induced transition dipole moment at the Cs–Xe distance  $R$ , and  $V_g$  and  $V_e$  the potentials of the ground and excited states, respectively. The temperature  $T$  is 371 °C according to the experimental condition of Moe et al. [1].

Fig. 1 shows the potential energy curves of the Cs–Xe system calculated by the SAC-CI method. We have calculated the ground and excited states which are correlated to the 6S(ground), 6P, 5D and 7S states of the Cs atom. Within the several basis sets examined here, we failed in getting a proper ordering of the 5D and 7S states of the Cs atom. So in fig. 1 the potential curve of the 7s $\Sigma$  state is shifted upwards, in order to avoid an overlap with the 5D state. The excitations to the 5D and 7S states are dipole forbidden in an atomic limit, but their intensities are

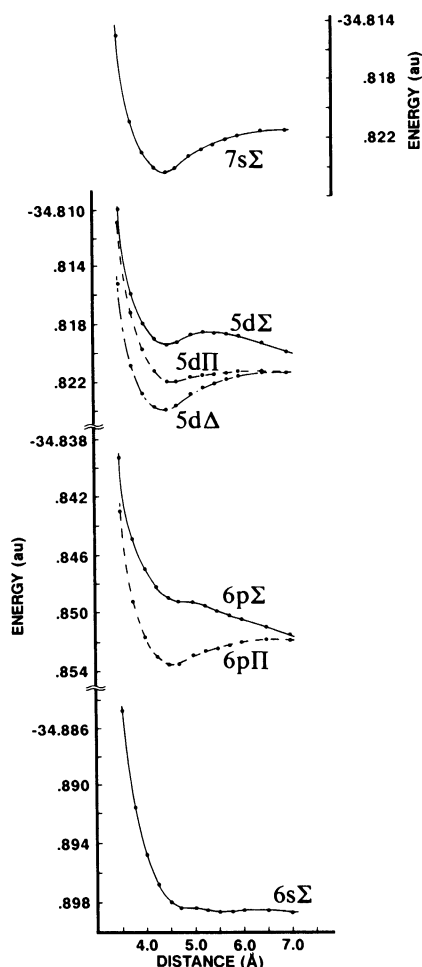


Fig. 1. Potential energy curves for the 6S, 6P, 5D and 7S states of Cs–Xe without including spin–orbit coupling. The potential curve of the 7s $\Sigma$  state is shifted upwards as noted in the text.

induced through the Cs–Xe interaction. The 5D state of the Cs atom splits into  $\Sigma$ ,  $\Pi$ , and  $\Delta$  states by the interaction, while the 6P state into  $\Sigma$  and  $\Pi$  states. The 6p $\Sigma$  and 5d $\Sigma$  states have a repulsive nature at large internuclear distances, and show a characteristic shoulder or hump near 5.0–5.5 Å. On the other hand, the 6p $\Pi$ , 5d $\Pi$ , 5d $\Delta$  and 7s $\Sigma$  states are attractive and have a shallow minimum near 4.5 Å. These two features of the potential curves are reflected in the positions and the profiles of the induced absorption spectra.

Fig. 2 gives induced dipole moments as a function

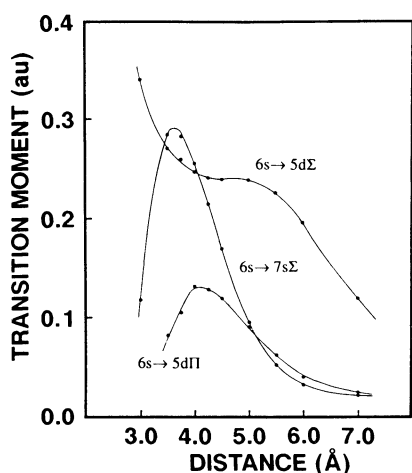


Fig. 2. Dependence of transition dipole moments on the Cs-Xe distance for the 6S-7S and 6S-5D transitions.

of the internuclear distance. The transitions from 6s  $\Sigma$  to 7s  $\Sigma$ , 5d  $\Sigma$  and 5d  $\Pi$  are induced at the intermediate nuclear distances of 4.3–7 Å, since the Boltzmann factor for the ground state sharply decreases at shorter distances than 4.3 Å. The 5d  $\Delta$  transition is dipole forbidden even after the interaction. The transition moment for the 5d  $\Sigma$  state is larger than those for the 7s  $\Sigma$  and 5d  $\Pi$  states. This is reflected in the intensity of the observed induced absorption spectra shown below.

The present theoretical absorption spectra for the 5D states are compared with experiment in fig. 3. The 6S-5D transition energy of the Cs atom is calculated at 588 nm in comparison with the experimental value of 692 nm. Though this difference of 0.303 eV is not small, the essential features of the spectra seem to be properly reproduced. The experimental peak in the blue region of the atomic-forbidden transition is attributed to the transition from the 6s  $\Sigma$  state to the 5d  $\Sigma$  state of the collision complex. The experimental band has a steep cusp, and correspondingly, the calculated band also shows a steep peak, which is due to the extremum in the excitation-energy dependence on  $R$ . In the quasistatic theory, the absorption intensity diverges at this extremum [5,11]. Looking at the potential curves, we see that this extremum is due to the hump of the 5d  $\Sigma$  potential shown in fig. 1, so that the cusp in the spectrum is assigned as being due to the hump of the 5d  $\Sigma$  potential. In the theoretical spectra,  $R$  denotes, in a

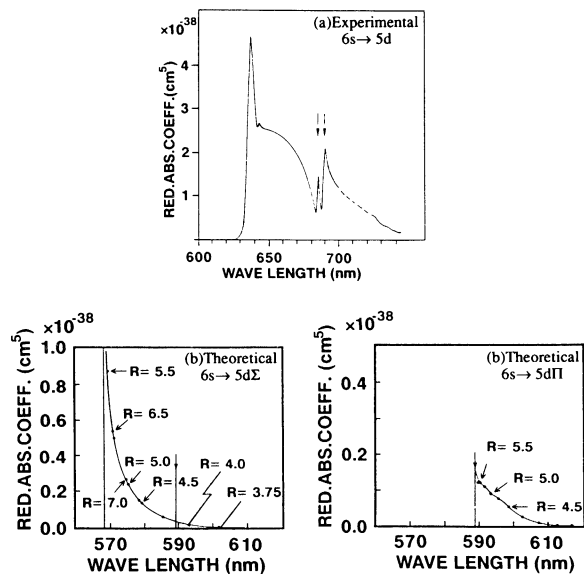


Fig. 3. (a) Experimental [1] and (b) theoretical reduced absorption coefficients for the 6S-5D transitions. In the theoretical spectra,  $R$  denotes the Cs-Xe distance in Å.

classical picture, an internuclear distance of the collision complex at which the absorption of the light of a given wavelength occurs. The experimental spectra have a broad shoulder at 650–670 nm, but the theoretical spectra do not have such a feature. So we do not know the origin of this shoulder. Though the calculated intensity of the spectra is about an order of magnitude smaller than the experimental one, the experimental determination of the intensity itself is rather difficult. Our intensity is similar to the theoretical one due to Sayer et al. [11].

The present result shows that the 6s  $\Sigma$ -5d  $\Pi$  transition would appear in a red region of the atomic-forbidden absorption. The calculated profile shown in the right-hand side of fig. 3 compares well with the experimental profile observed in the red region of the forbidden line shown by the arrows (two arrows indicate spin-orbit splitting). In this red region, the 6s  $\Sigma$ -5d  $\Sigma$  transition also contributes as shown in the left-hand side of fig. 3. However, the absorption intensity of this transition in the red region is small because the Boltzmann factor of the ground state in the region  $R < 4.0$  Å is very small. The experimental profile is the sum of the 6s  $\Sigma$ -5d  $\Pi$  and 6s  $\Sigma$ -5d  $\Sigma$  transitions, the former being the main contribution.

In fig. 4 we compare the experimental and theo-

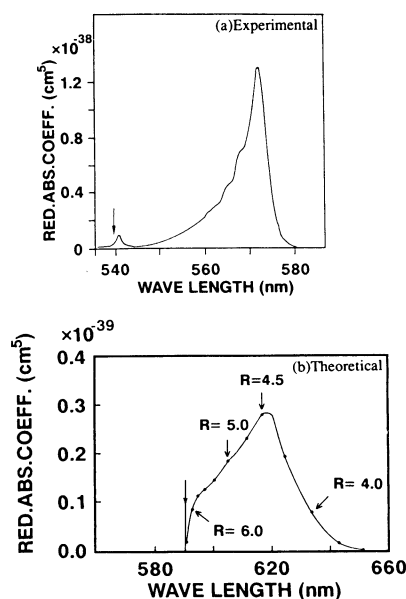


Fig. 4. (a) Experimental [1] and (b) theoretical reduced absorption coefficients for the 6S–7S transition. In the theoretical spectrum,  $R$  denotes the Cs–Xe distance in Å.

retical collision-induced absorption spectra associated to the 6S–7S transition of the Cs atom. The experimental spectrum [1] has a vibrational structure which indicates an existence of an attractive potential well for the excited state. The depth of the potential well of the  $7s\ \Sigma$  state shown in fig. 1 is 0.078 eV. The position of the calculated atomic forbidden transition differs by 0.196 eV from the experimental value. Both experimental and theoretical induced absorptions appear in the red region of the atomic transition, though the shapes of the profiles are somewhat different. The induced transition moment should increase more rapidly as the Cs–Xe distance becomes smaller. At shorter distances, the Boltzmann factor of the ground state rapidly diminishes, so that the induced absorption intensity falls off very rapidly.

More details of the present study and the results for the 6S→6P transitions will be published elsewhere.

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## References

- [1] G. Moe, A.C. Tam and W. Happer, *Phys. Rev. A* 14 (1976) 349.
- [2] A.C. Tam, G. Moe, B.R. Bulos and W. Happer, *Opt. Commun.* 16 (1976) 376.
- [3] A.C. Tam, G. Moe, W. Park and W. Happer, *Phys. Rev. Letters* 35 (1975) 85.
- [4] R.T.M. Su, J.W. Bevan and R.F. Curl Jr., *Chem. Phys. Letters* 43 (1976) 162.
- [5] J.F. Kielkopf and N.F. Allard, *Rev. Mod. Phys.* 54 (1982) 1103; P.R. Brooks, *Chem. Rev.* 88 (1988) 407.
- [6] A. Gallagher and T. Holstein, *Phys. Rev.* 16 (1977) 2413.
- [7] G. Alber and J. Cooper, *Phys. Rev. A* 33 (1986) 3084.
- [8] J. Pascale and J. Vandeplanque, *J. Chem. Phys.* 60 (1974) 2278.
- [9] W.E. Baylis, *J. Chem. Phys.* 51 (1969) 2665.
- [10] J. Pascale, *J. Chem. Phys.* 67 (1977) 204.
- [11] B. Sayer, J.P. Visticot and J. Pascale, *J. Phys. (Paris)* 39 (1978) 361.
- [12] H. Nakatsuji and K. Hirao, *J. Chem. Phys.* 68 (1978) 2053.
- [13] H. Nakatsuji, *Chem. Phys. Letters* 59 (1978) 362; 67 (1979) 329, 334.
- [14] H. Nakatsuji, *Chem. Phys.* 75 (1983) 425.
- [15] H. Nakatsuji, *Theoret. Chim. Acta* 71 (1987) 201.
- [16] Y. Mizukami and H. Nakatsuji, *J. Chem. Phys.* (1990), in press.
- [17] W.R. Wadt and P.J. Hay, *J. Chem. Phys.* 82 (1985) 284.
- [18] S.R. Langhoff, C.W. Bauschlicher Jr. and H. Partridge, *J. Phys. B* 18 (1985) 13.
- [19] W.C. Ermler, Y.S. Lee, K.S. Pitzer and N.W. Winter, *J. Chem. Phys.* 69 (1971) 716.
- [20] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, *Gaussian basis sets for molecular calculations* (Elsevier, Amsterdam, 1984).
- [21] B.R. Brooks, P. Saxe, W.D. Laidig, and M. Dupuis, *Program System GAMESS, Program Library No. 481, Computer Center of the Institute for Molecular Science* (1981).
- [22] H. Nakatsuji, *Program system for SAC and SAC-CI calculations, Program Library No. 146 (Y4/SAC), Data Processing Center of Kyoto University* (1985); H. Nakatsuji, *Program Library SAC85 (No. 1396), Computer Center of the Institute for Molecular Science, Okazaki* (1986).
- [23] J. Holmtzmark, *Ann. Phys. (Leipzig)* 58 (1919) 577.
- [24] A. Jablonski, *Phys. Rev.* 68 (1945) 78.
- [25] S.Y. Chen and M. Takeo, *Rev. Mod. Phys.* 29 (1957) 20.