

High Resolution Study of H_2 in the Vacuum-uv Region
:Line Profile of the $3p\pi D^1\Pi_u - X^1\Sigma_g^+$ bands

Sanzo TAKEZAWA AND Yoshihiro IIDA
College of Medical Care and Technology
Gunma University
Showamachi, Maebashi, Gunma 371
(Received in September 30, 1988)

Summary

The diffuse profiles of P and R lines in the D-X system of H_2 are investigated in connection with the other electronic states interacting with the D state by high resolution spectroscopy. Previously it has been widely claimed that the predissociation of the Π^+ substate of $3p\pi D^1\Pi_u$ occurs at the $v = 3$ level and above. The dissociating energies of the $2p\sigma B^1\Sigma_u^+$, $3p\sigma B'^1\Sigma_u^+$, and $2p\pi C^1\Pi_u$ states $H(1s)+H(2s,2p)$ correspond to those between the $v = 2$ and 3 levels of the D state. Among of them the state, mostly responsible to the predissociation, is considered to be the B' state. The theoretically calculated potentials of the B' and D states assert the slightly decreased interactions with the growing v' at the $J = 1$ levels of D for $v = 3-12$. It is much preferable for the examination of the theoretical prediction to study the line profiles with high J. So far the investigation about D-X has been limited mostly to R(0) and R(1). We focus the study on the R(J) lines with $J = 2$ and 3 for $v' \geq 6$. Consequently, the slightly increased line widths with the growing v' are found against the theoretical prediction.

<Key Words> Line Profile, H_2 , $3p\pi$ D State

Introduction

It has been widely known that the absorption bands of D-X bands with $v' = 3$ and above become diffuse in the P and R branch lines, but not in the Q branch lines. This phenomenon has been interpreted in terms of a predissociation effect; Beutler-Fano

line profile (1,2), similar to an autoionization, results from mixing of continua and discrete levels. The $2p\sigma$ $B^1\Sigma_u^+$, $3p\sigma$ $B'^1\Sigma_u^+$, and $2p\pi$ $C^1\Pi_u$ states dissociate into $H(1s)+H(2s,2p)$. These dissociated energies correspond to those between $v = 2$ and 3 of the $3p\pi$ D state. A predissociation, therefore, occurs at the levels $v = 3$ of the D state and above. Also, this predissociation effect has been supported by the missing emission bands with $v' = 3$ level and above.

Previously several workers, including one of the authors, studied the D-X bands by means of high resolution spectroscopy (3-10). The rotational analysis, however, has been still obscure and not completed excepted for those with $v' = 0 - 3$. The precise line assignments for this region, including the D-X bands, are a difficult matter, because of numerous overlapped Rydberg bands. Especially, the ($v' \geq 6,0$) bands are under the influence of the autoionization as well as the predissociation; the limit of the (0,0) Rydberg series, $124\,417.2\text{ cm}^{-1}$ (15.426 eV), corresponds to the first ionization potential of H_2 . The (6,0) band used to be referred as a typical example of a rotational autoionization, but presently it has been denied; the line diffuseness is ascribed to a predissociation, not a autoionization. Also, the theoretical calculation predicts the decreasing line widths of the D-X bands with the increasing v' (11,12). To date no one has studied the diffuse line profiles enough to examine the theoretical calculations.

The purpose of this article is to study the diffuse line-profiles of the D-X bands, especially of the R branch with high J and to throw light upon the interaction between the B' and D states by high resolution spectroscopy.

Experimental

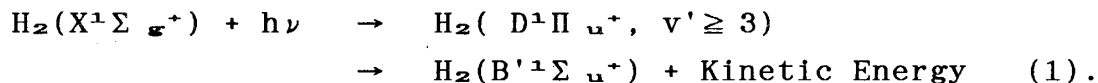
The photographic plates used in this work was obtained by the spectrograph described in the previous work(6,13). In brief, the spectrum was taken by using the second order of the 6.65m normal incidence spectrograph with the reciprocal dispersion of 0.6 A/mm on the plate . A windowless absorption cell of about

20cm length was used in combination with the helium continuum as a background light source.

Discussion and Results

A. Theoretical background of line diffuseness in the D-X bands.

Figure 1 shows potential curves of H_2 . As illustrated in the figure, the $2p\sigma$ B, $3p\sigma$ B', and $2p\pi$ C states dissociate to $H(1s) + H(2s,2p)$, which locates at the place between the $v = 2$ and 3 levels of $3p\pi$ D. When the selection rules of autoionization are applied to the case, the dissociation continua of the $B^1\Sigma^+$, $B'^1\Sigma^+$ states and the $^1\Pi^+$ substate of C can predissociate the Π^+ substate of D. Also, that of the Π^- substate of C may predissociate the Π^- substate of D. The strongest interaction should be that between the B' and Π^+ substate of D, because the potential curves of the B' and D states are expected to be closer in the left side than those of B and D or C and D. Thus the following process plays an important role in the line profiles.



We, therefore, could interpret the Q lines of D-X as being sharp and the P and R lines as diffuse; $\Sigma^+ - \Pi^+$ and $\Pi^- - \Pi^-$ interactions give influence to P and R, and to Q, respectively.

Julienne(9) calculated the half-widths at $J = 1$, $\Gamma(D, B')$, $\Gamma(D, B)$ and $\Gamma(D, C)$, from the potential curves of C, D, B, and B' and from the Born-Oppenheimer coupling term (14)

$$V = (m/2\mu) [J(J+1)] F(R)/R^2, \quad (2)$$

where $F(R)$ is electronic matrix elements in the $\Pi - \Sigma$ interaction. The values of $\Gamma(D, B')$ were found to be 1.18 cm^{-1} for $v = 1$, 1.12 for $v = 2$ and 0.67 for $v = 12$. As expected, $\Gamma(D, B)$ and $\Gamma(D, C)$ were about 1/1000 times of $\Gamma(D, B')$. Also, Fiquet-Fayard and Gallais(12) claimed from their theoretical calculation much larger line widths than those by Julienne for the D-X bands with $v' = 3, 4$ and 5; they were $4.8, 4.7, \text{ and } 4.6 \text{ cm}^{-1}$ for $v' = 3, 4$ and 5. The disagreement between the two calculations were remarkable.

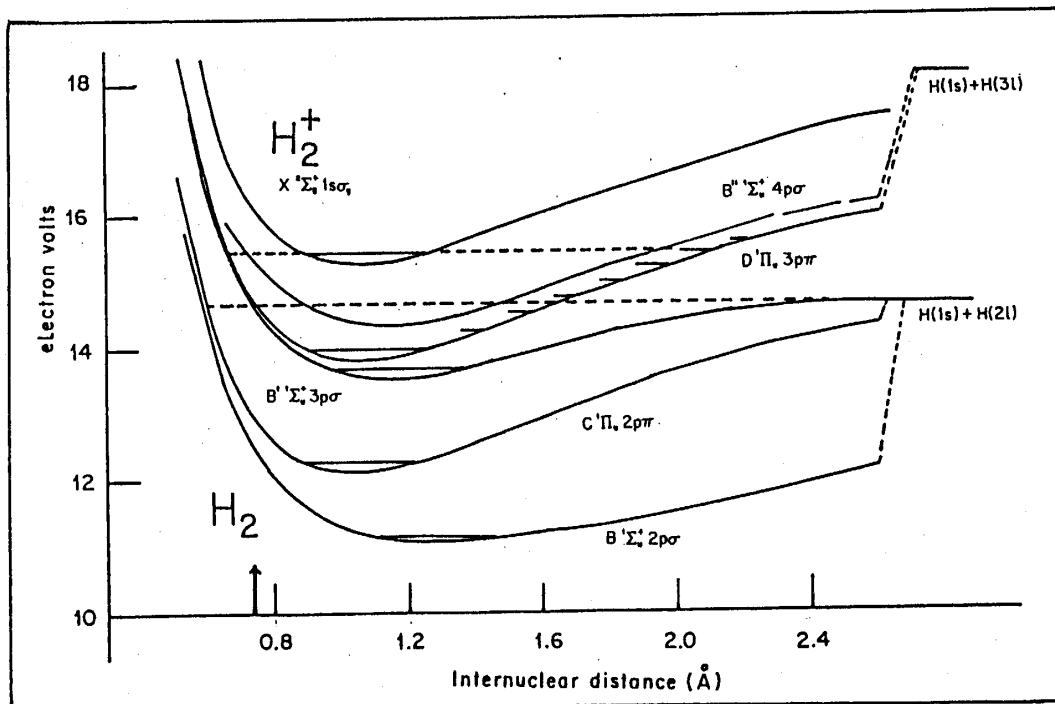


Figure 1. Potential curves of $2p\sigma$ B', $3p\sigma$ B'', $2p\pi$ C and $3p\pi$ D states. The arrow in the bottom indicates the internuclear distance of the ground state, $1s\sigma$ $X^1\Sigma_g^+$, in the neutral H_2 .

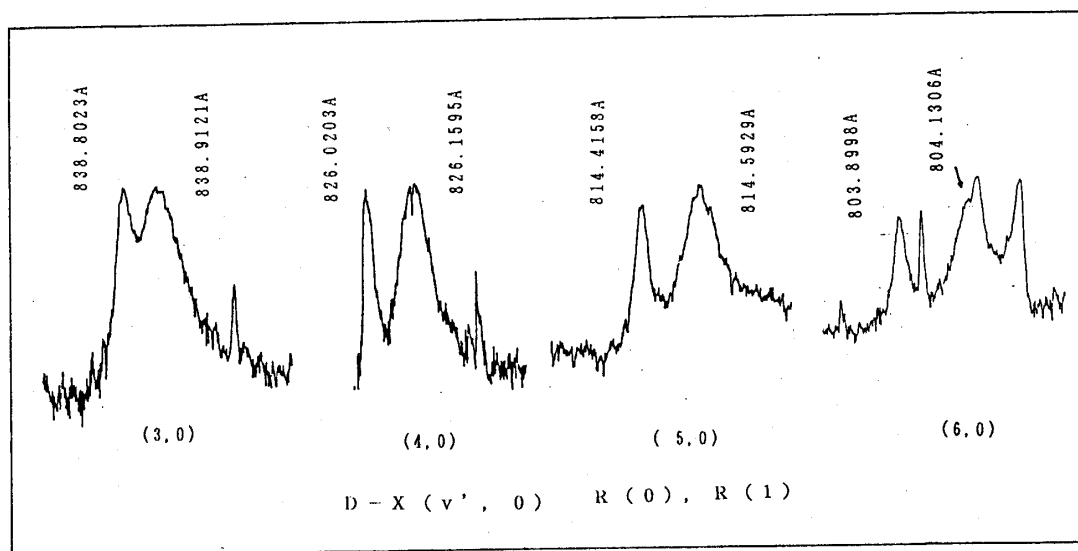


Figure 2. The densitometer traces of the diffuse R(0) and R(1) absorption lines in the D-X(v' , 0) bands with $v' = 3 - 6$.

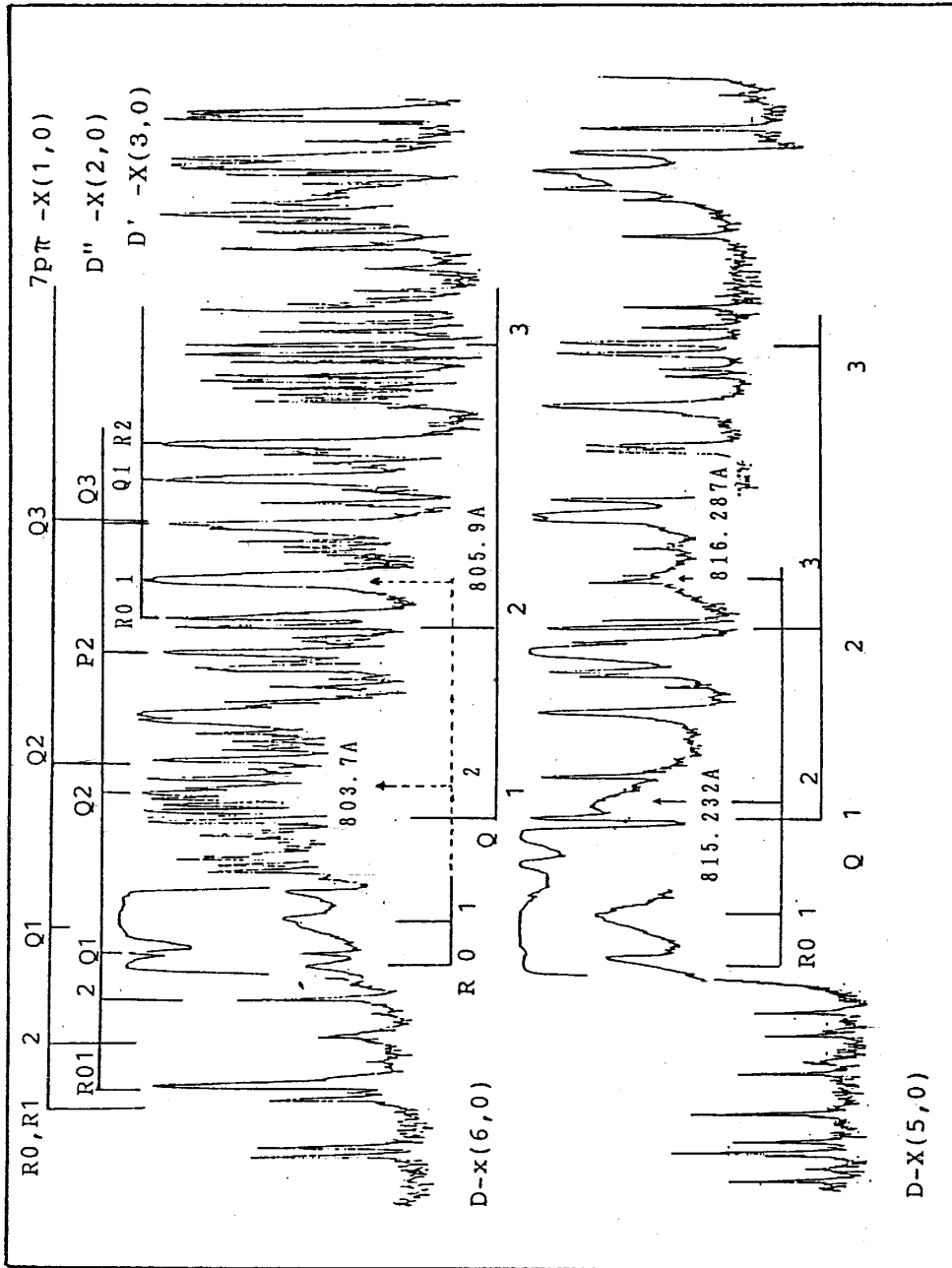
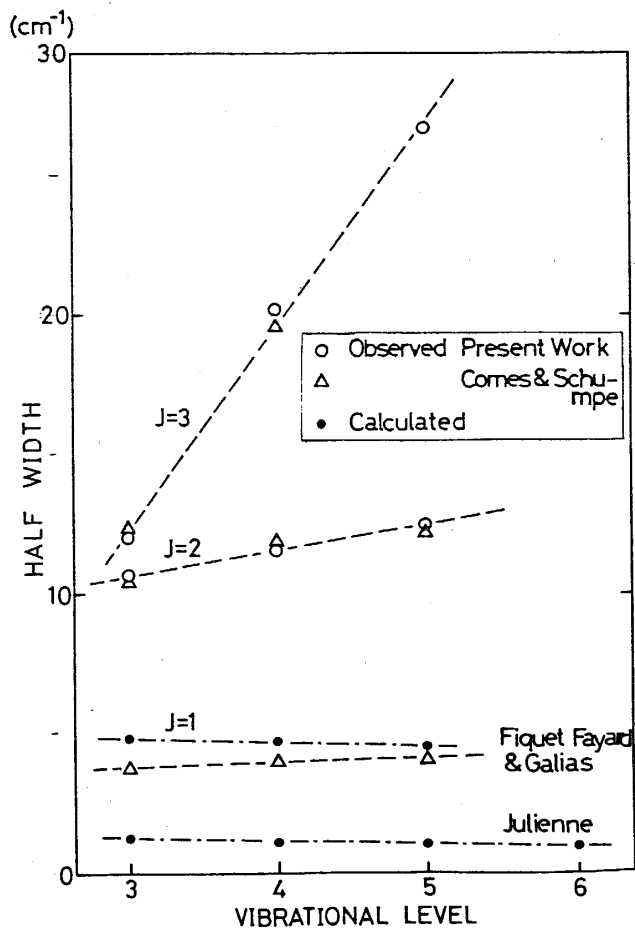
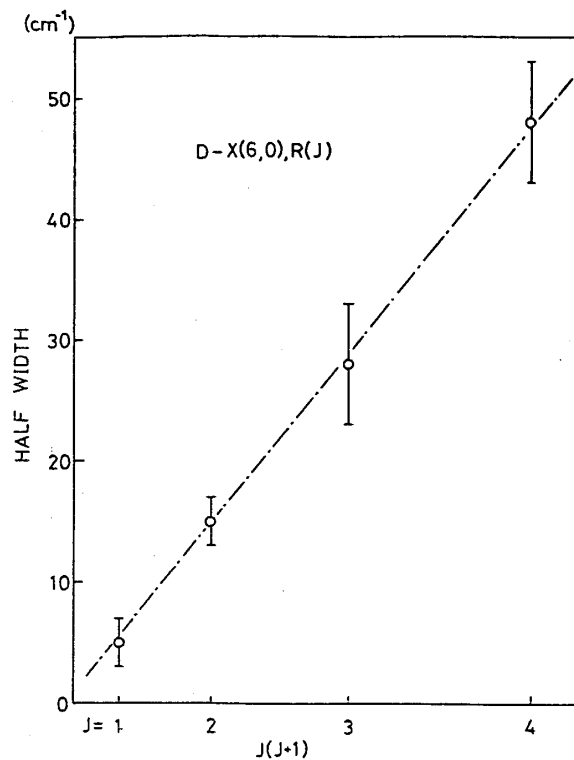


Figure 3. The densitometer traces in the regions, 802-806 and 814-818 A, in which the D-X(6,0) and D-X(5,0) bands are, respectively, observed. The diffuse R(J) lines are indicated with arrows. The only part of line assignments are shown in the figure.



(a)



(b)

Figure 4. a) The line widths of the diffuse R(0), R(1), R(2) and R(3) lines in D-X($v'=3,4,5, v''=0$) against $J'(J'+1)$. Solid circles for R(0)($J'=1$) indicate the calculated ones by Fiquet-Fayard and Galias (Ref.12) and by Julienne(Ref.11), respectively. Triangles are the observed values by Comes and Schumpe (Ref.10).

b) The presently observed line widths of R(0),R(1),R(2),and R(3) for D-X(6,0) against v' . Vertical lines indicate the estimated measurement errors in this work.

In the both case, however, the values indicated a tendency of slight decrease in the line widths with the increasing v' . If true, this trend is very interesting, because in general the potentials of Rydberg states should gradually approach and become closer on the left sides in proportion to potential energy. Since the D and B' states have different Rydberg electrons $4p\pi$ and $3p\sigma$, respectively, the calculated tendency mentioned above may be possible. However, the difference between those for $v'=3$ and 6 is only 0.06cm^{-1} , which is too small to examine the prediction experimentally. Fortunately the coupling term of Eq.(2) includes square root of $J(J+1)$. It, therefore, is undoubted that the lines with high J have the advantage of the investigation on the line profiles. Unfortunately the previous work has failed to observe such lines with high J except for a few lines and has been limited to the observation of the R(0) and R(1) lines; they are remarkably intense and reveal the characteristic profiles.

B. Line profiles of P and R lines in the D-X ($v' \geq 3$) bands.

Figure 2 shows the profiles of R(0) and R(1) lines in the (3,0) - (6,0) bands. To measure the line widths from the densitometer traces of photographic plates is a difficult matter and may be not always precise. Nevertheless, it is hard in this work to estimate the concrete growing variation of the line widths from the densitometer traces in this work. Thus this work was focused to find the lines with high J.

Figure 3 shows the densitometer traces of the absorption spectra in this work. The upper and bottom ones, respectively, correspond to the wavelength regions 802-805 and 810-815A, in which the D-X(5,0) and D-X(6,0) bands were observed. The presently concerned rotational lines are indicated with solid lines in the figure. As seen in figure, the P and R lines are remarkably broad in the bands with above $v'=3$. On the other hand, the Q lines remain their profiles sharply. The very broad absorption lines R(2), R(3) and P(2) of D-X(5,0) were observed, when the absorptions of R(0) and R(1) lines saturated because of the high pressure of the sample gas. The R(3) and P(2) lines were

observed for the first time in this work. Their profiles are much more diffuse than those of R(0) and R(1), and also the peaks of intensities are considerably lower. The observation of the R(2) or R(3) lines with $v'=6$ and above is desirable to the present purpose. Although we attempt to use a pressure of hydrogen gas as practically high as possible, the diffuse lines mentioned above were not distinctly found. The observation was disturbed by numerous lines of the many overlapped Rydberg bands. The (0,0) Rydberg series converge to the first ionization potential; the $v=0$ level of the H_2^+ ground state $X^1\Sigma_g^+$ is 124417.2 cm^{-1} (15.4258 eV).

As seen in the upper trace of Fig. 3, however, the broad R(2) line of the (6,0) band seems to be immersed into many absorptions near the Q(2) line of $D''-X(2,0)$ band; it is around 803.7 Å. Also the position of the R(3) line is expected near the R(1) line of the $D'-X(3,0)$ band (805.9258 Å). It is the broad and strong line as indicated with the arrow in Fig. 3. This line is not concerned with a autoionization or a predissociation; the $D'(v=3)$ state locates below the ionization potential. Consequently, this R(1) line should not be such a diffuse and strong line. Thus the R(3) line of $D-X(6,0)$ may be superimposed upon the R(1) line of $D'-X(3,0)$. We can speculate those lines to be broad shapes and to be immersed into many absorption lines or strong line mentioned above.

In Fig.4a and 4b, the presently measured line widths are shown together with ones by Comes and Schumpe(10) and the theoretically calculated ones ($J=1$) by Julienne (11) and by Fiquet-Fayard and Galias (12). Previously Comes and Schumpe observed the diffuse R(0),R(1),R(2) for $v'=3, 4$ and R(0) and R(1) for $v'=5$. Their values are indicated with the symbols " Δ " in the figur. Although they used the photometric method different to the photographic one in this work, their values agree with the present ones within experimental errors; the present values are indicated with symbols " \circ ". The theoretical calculation by Fiquet-Fayard and Galias(12) is about four times larger than that of Julienne(11). Julienne's calculation seems to be too small;it

was caused from missing factor in the formulation and from use of the inaccurate RKR potentials. Either way it is important that the trend of the both calculation is slight decrease of the line widths with increasing v' ; the both ones are indicated with "●" in Fig. 3. As understood in Fig. 4b the measurements by Comes and Schumpe (6) as well as the present ones at $J=1$ are not enough to examine the theoretical prediction; the difference between the measured and calculated widths is within the experimental error. The tendency of increase in the half widths with the growing v' is not clear for even $J=2$. From the present observation for $J=3$, however, the increasing widths with v' will be obvious, even though the large estimated error arising from a photographic method must be taken into account(see Fig. 4b). Unfortunately the R(3) line was found only in the (5,0) band(see Fig. 4a). We, however, may presume the large interaction even at $J=4$.

Conclusion

The theoretical calculation for line widths of the D-X bands has asserted the gradual decrease of predissociation widths with the enhanced v' . As the previous measurements were limited to R(0) and R(1) of the bands, its examination was experimentally difficult. Contrary to the theoretical prediction, it is concluded by the observation of R(3) and R(4) in this work that the predissociation widths of the D-X bands increase slightly with the increased v' , and consequently, the potentials of D' and B' should be closer in proportion of the growing energy. In future, however, it is required to observe the R or P lines with high J of bands with $v'=6$ and above, which will give the more concrete evidence about the line widths. From the spectrum cooled at liquid nitrogen temperature, the identification of the lines with $J''=0$ and 1 is undoubted in this region, but the ones with high J'' is not yet precise. The use of parahydrogen will be preferable to eliminate the absorption lines with odd J'' and will make the identification of the lines easier. Also, the accurate measurement of line widths by means of high resolution photometric method is required. The theoretical study on the precise poten-

method is required. The theoretical study on the precise potential curves, especially the D and B' states, will be essential to the investigation of the line profiles in the D-X bands.

References

1. Beutler, H. and Junger, H.O., Physik **100**: 80-87, 1936.
2. Fano, U. and Cooper, J.W., Phys. Rev. **137A**:1364-1379, 1961.
3. Monfils, A., J. Mol. Spectrosc. **25**: 513-543. (1968).
4. Namioka, T., J. Chem. Phys. **40**: 3153-3162, 1964.
5. Namioka, T., J. Chem. Phys. **41**: 2141-2156, 1964.
6. Takezawa, S., J. Chem. Phys. **52**: 2575-2590, 1970.
7. Takezawa, S., J. Chem. Phys. **52**: 5793-5798, 1970.
8. Herzberg, G. and Jungen, Ch., J. Mol. Spectrosc. **41**: 425- 1972.
9. Dehmer, P. A. and Chupka, W. A., J. Chem. Phys. **65**: 2243-2273, 1976.
10. Comes, F. J. and Schumpe, G., Z. Naturforsch, **26a**: 538-546, 1971.
11. Julienne, P. J., Chem. Phys. Letters **8**: 27-28, 1971.
12. Fiquet-Fayard, F. and Galias, O., Chem. Phys. Letters, **16**: 18-19, 1972.
13. Takezawa, S., Ann. Rep. Med. Care Technol. Gunma Univ. **2**: 107-116, 1981.
14. Kolos, W. and Wolniewicz, L., Rev. Mod. Phys. **35**: 473-485, 1963.