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MOLECULAR RYDBERG TRANSITIONS IN CARBON MONOXIDE:
TERM VALUE/IONIZATION ENERGY CORRELATION OF BF, CO AND N₂

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IONIZATION ENERGY CORRELATION OF BF, CO AND N₂ *

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Abstract

The linear correlation between the term value and ionization energy for molecular Rydberg transitions is tested for the sequence of isoelectronic molecules BF, CO and N₂ based on a new measurement of the absorption spectrum of CO and data for BF and N₂. For the np^σ series and np^π series converging on the first ionization potential, we find an excellent linear behavior (within 10 meV) corroborating (i) the correlation and (ii) the individual assignments. For Rydberg series leading to the A²Π and B²Σ⁺ states, where no data for BF are available, a comparison of term values for CO and N₂ is presented.

Introduction

For many molecules the interpretation and correct assignment of the vacuum ultraviolet absorption spectrum is tedious due to the large number of occupied valence orbitals and the many accessible states which usually overlap heavily in the absorption spectrum. Fortunately, quite frequently a large number of absorption bands can be arranged in hydrogenic-like Rydberg series according to the well known Rydberg formula

$$E_{n\alpha} = IP^k - \frac{R}{(n - \delta_{n\alpha})^2} \quad (1)$$

where $E_{n\alpha}$ is the energy of the n th member of the α^{th} Rydberg series converging on the k^{th} ionization potential IP^k . R denotes the Rydberg constant (13.6055 eV for CO) and $\delta_{n\alpha}$ is a quantum defect characteristic for the symmetry of the Rydberg series {1, 2}.

A certain routine has been developed in the past few years for making assignments with more confidence; but, with more and more experimental data becoming available, it is apparent that in many cases much remains to be done to arrive at satisfactory assignments {3}. In an ideal situation long non-overlapping series are observed yielding unequivocal assignments {1, 4}. For many molecules comparison with a highly resolved photoelectron spectrum and with a good quantum-chemical calculation for the ground state has provided key information about the orbitals from where the transitions originate and a guideline for the interpretation of vibrational progressions associated with the Rydberg transition {2, 3, 5}.

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The next important step is the ordering of the observed bands into ns, np, nd ... type Rydberg series {2, 6}. A powerful tool for the further analysis is the comparison of equal members of corresponding Rydberg series within a group of related molecules as demonstrated convincingly by Robin {2}. This method has been given a quantitative formulation by Maria et al. {7} who found a linear relationship between the excitation energies or term values of the Rydberg transitions and the corresponding ionization potentials. This relationship can be written in the form {8}

$$T_{n\alpha} = a_{n\alpha} \cdot IP^k + b_{n\alpha} \quad (2)$$

where $a_{n\alpha}$ and $b_{n\alpha}$ are constants for a certain Rydberg series and a certain member n within a set of related molecules, and $T_{n\alpha}$ is the term value

$$T_{n\alpha} : = IP^k - E_{n\alpha} \quad (3)$$

This linear term value ionization energy correlation has been successfully tested for atoms and several groups of molecules by Hochmann and McGlynn and their coworkers {8, 9}. An obvious advantage of this method is that it can be used even if only very few Rydberg states are known and especially for series members of low n for which often the most significant deviations from a constant quantum defect are observed. It is however not clear a priori what kind of relatedness is necessary in the group of molecules one chooses for a comparison.

It is of interest to further test this relationship for simple molecules and probe the limits of its applicability by using high resolution

absorption spectra. In the present work we apply equation (2) to the Rydberg series of the sequence of molecules BF, CO and N₂. The relation of these molecules is that they are isoelectronic but have a quite different geometry of the total electron density since for both constituting atoms the nuclear charge is changed by one in each step going through the sequence. Thus we investigate for these simple molecules the influence of the molecular geometry while keeping the number of valence electrons constant. The test is based on data from our new measurements of the absorption spectrum of CO, the previously determined absorption spectrum of the BF molecule by Gatton and Douglas {10} and our previous measurement of the N₂ absorption spectrum {11, 12}.

Experimental Details

The absorption spectrum of CO has been measured by the use of synchrotron radiation from the electron-positron storage ring DORIS at DESY in Hamburg dispersed by a high resolution scanning monochromator {13}. This made possible photoelectric recording of the spectra with a resolution of $\Delta\lambda \leq 0.015$ nm in the photon energy range $7 \text{ eV} \leq h\nu \leq 25 \text{ eV}$. As sample gas we used high purity CO gas (99.997%) from l'Air Liquide in a windowless gas cell. The transmitted photons were converted by sodium salicylate into light with longer wavelength and detected by an EMI 9804 photomultiplier. The full CO absorption spectrum together with more details of the experiment will be published elsewhere {14}.

Results and Discussion

In Fig. 1 those parts of the CO spectrum are displayed which contain the $5\sigma \rightarrow n\pi$ (0,0) and $5\sigma \rightarrow n\pi$ (0,0) Rydberg transitions. Our assignment closely follows the previous analysis as reported by Ogawa and Ogawa [15]. For $n \geq 6$ both series coalesce and no separate maxima are observed. The excitation energies E_n of these two series converging to the $X^2\Sigma^+$ state as well as those belonging to Rydberg transitions converging to the $A^2\Pi$ and $B^2\Sigma^+$ states, respectively, are compiled in Tables 1, 2 and 3. In Table 1 the energies E_n values for the quantum defect δ_n , the first ionization potential IP^1 and the term values T_n of the first 7 members of the Rydberg-series $5\sigma \rightarrow n\pi$ (0,0) and $\rightarrow n\pi$ (0,0) are compared to those for BF and to those for the corresponding series $3\sigma_g \rightarrow n\pi_u$ (0,0) and $\rightarrow n\pi_u$ in N_2 . As for CO the $n \geq 6$ transitions coalesce in N_2 and no separate peaks have been observed. The data of BF were taken from the high resolution work of Caton and Douglas [10] where we used the relationship E_n (eV) = $1.239852 \times 10^{-4} \tilde{\nu}_n$ (cm^{-1}) to convert the originally published data into eV. For N_2 we took the data from Gürtler et al. [11, 12]. They were obtained previously with the same experimental setup as used in the present study.

In Fig. 2 a plot of T_n versus the ionization energy IP^1 , as given in Table 1 for the Rydberg transitions $n = 3$ to $n = 9$ is shown for the three molecules. The linear correlation as predicted by equation 2 is obvious. This is especially remarkable for the lower members of both the $n\pi$ and $n\pi$ Rydberg series. Here, within 10 meV the data

points follow the linear behavior. The result clearly shows the applicability of equation 2 to a group of isoelectronic molecules, i.e. a linear relationship between the Rydberg term values and corresponding ionization limits. The slope of the correlation lines, especially for $n = 3$, reflects the influence of the decreasing asymmetry of the total electron density from BF towards N_2 . This asymmetry also causes the large π and π splitting which is almost negligible for N_2 . Furthermore, our result is a strong argument in favor of the correctness of individual assignments in all three substances. In order to study this relationship in more detail a comparison of other Rydberg states and application of equation 2 to molecular groups like e.g. CO, SiO and GeO as cross check would be desirable, but to our knowledge experimental results so far are not sufficient for this purpose.

A further question remains: How, if at all, can this relation be transferred to Rydberg excitations of the same molecules originating from more tightly bound valence orbitals? In the absence of data for BF we compare the observed term values of Rydberg series converging to the second and third ionization potential in CO and N_2 . The results are compiled in Tables 2 and 3. As expected the difference in term values ΔT_n decreases with increasing n . For $n = 3$ the difference of 0.245 eV for the $1\pi \rightarrow n\sigma$ in CO and $1\pi_n \rightarrow n\sigma_g$ in N_2 is large although the values for the ionization potentials are quite close.

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TABLES 2a, 2b:

Energies E_n , quantum defects δ_n , term values T_n and ionization potentials IP for the Rydberg series converging to the second IP's in CO and N_2 . In Table 2a the series $1\pi \rightarrow n\sigma(0,0)$ in CO is compared to the corresponding $1\pi_u \rightarrow n\sigma_g(0,0)$ series in N_2 . In Table 2b the series $1\pi \rightarrow n\sigma(0,0)$ in CO is compared to the corresponding $1\pi_u \rightarrow n\sigma_g(0,0)$ series in N_2 . $\Delta T_n = T_n(CO) - T_n(N_2)$ denotes the differences of the term values for corresponding Rydberg states.

TABLE 2a:

n	CO			N_2 (a)			ΔT_n (eV)
	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)	
3	12.7485	1.11	3.805	13.1021	1.06	3.560	0.245
4	14.9784	1.06	1.575	15.1468	1.04	1.555	0.020
5	15.6737	1.06	0.879	15.8187	1.07	0.883	-0.004
6	15.9936	1.06	0.559	16.1447	1.06	0.557	0.002
7	16.1658	1.06	0.387	16.3179	1.05	0.384	0.003
8	16.2676	1.07	0.285	16.4212	1.03	0.281	0.004
9	16.3308	1.14	0.222	16.4869	1.04	0.215	0.007
10	16.3813	1.04	0.172	16.5328	1.02	0.169	0.003
IP	16.553			16.702			

TABLE 2b

n	CO			N_2			ΔT_n (eV)
	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)	
3	14.8304	0.19	1.723	15.0176	0.16	1.685	0.038
4	15.6153	0.18	0.938	15.7722	0.18	0.931	0.007
5	15.9631	0.18	0.590	16.1189	0.17	0.584	0.006
6	16.1492	0.16	0.404	16.2993	0.19	0.404	0.000
7				16.4128	0.15	0.290	
8	16.3259	0.19	0.227	16.4804	0.18	0.223	0.004
IP	16.553			16.703			

(a) Data from reference (12, 13)

TABLE 1: Energies E_n , quantum defects δ_n , term values T_n and ionization potentials IP for the Rydberg series $5\sigma \rightarrow n\pi(0,0)$, $\rightarrow n\pi^+(0,0)$ in BF and CO and for the corresponding $3\sigma_g \rightarrow n\pi\sigma_u(0,0)$, $\rightarrow n\pi\pi_u(0,0)$ series in N_2 .

n	BF (a)			CO			N_2 (b)		
	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)
3 σ	8.5717	0.69	2.543	11.3969	0.72	2.617	12.9326	0.73	2.648
π	8.9624	0.49	2.153	11.5224	0.66	2.492	12.9084	0.74	2.673
4 σ	9.8895	0.67	1.226	12.7780	0.68	1.236	14.3584	0.66	1.223
π	10.0034	0.50	1.112	12.8069	0.64	1.207	14.3302	0.70	1.251
5 σ	10.3922	0.66	0.723	13.2869	0.68	0.727	14.8610	0.65	0.720
π	10.4417	0.51	0.673	13.2941	0.65	0.720	14.8467	0.70	0.734
6 σ	10.6386	0.66	0.476	13.5386	0.65	0.475	15.0999	0.68	0.481
π	10.6650	0.50	0.450						
7 σ	10.7770	0.66	0.338	13.6790	0.63	0.335	15.2541	0.55	0.327
π	10.7914	0.52	0.324						
8 σ	10.8628	0.66	0.252	13.7630	0.64	0.251	15.3295	0.65	0.252
π	10.8708	0.54	0.244						
9 σ	10.9199	0.66	0.195	13.8199	0.63	0.194	15.3847	0.68	0.196
π	10.9257	0.53	0.189						
IP	11.115			14.014			15.581		

(a) data from Reference (11)
 (b) data from Reference (12, 13)

TABLES 3a, b:

Energies E_n , quantum defects δ_n , term values T_n and ionization potentials IP for the Rydberg series converging to the third IP's in CO and N_2 . In Table 3a, the series $4\sigma \rightarrow n\sigma$ (0,0) in CO is compared to the corresponding $2\sigma_u \rightarrow n\sigma_g$ (0,0) series in N_2 . In Table 3b the series $4\sigma \rightarrow nd\sigma$ (0,0) in CO is compared to the corresponding $2\sigma_u \rightarrow nd\sigma_g$ (0,0) series in N_2 .

$\Delta T_n = T_n(\text{CO}) - T_n(\text{N}_2)$ denotes the differences of the term values for corresponding Rydberg states.

TABLE 3a:

n	CO			N ₂ (a)			ΔT_n (eV)
	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)	
3	16.3025	0.99	3.370	-	-	-	-
4	18.1986	0.97	1.473	17.3091	0.94	1.453	0.020
5	18.8467	0.95	0.825	17.9381	0.93	0.824	0.001
6	19.1382	0.97	0.534	18.2297	0.94	0.532	0.002
7	19.3015	0.97	0.371	18.3925	0.93	0.370	0.001
8	19.3975	1.00	0.275	18.4887	0.95	0.273	0.002
9	19.4606	1.04	0.211	18.5518	0.96	0.210	0.001
10	19.5046	1.07	0.167	18.5977	0.91	0.164	0.003
IP	19.672			18.762			

TABLE 3b:

n	CO			N ₂			T_n (eV)
	E_n (eV)	δ_n	T_n (eV)	E_n (eV)	δ_n	T_n (eV)	
3	17.9431	0.19	1.729	17.1298	0.11	1.624	0.105
4	18.7297	0.19	0.942	17.8420	0.14	0.912	0.030
5	19.0788	0.01	0.593	18.1733	0.16	0.581	0.012
6	19.2676	0.18	0.404	18.3572	0.15	0.397	0.007
7	19.3763	0.18	0.296	18.4639	0.16	0.290	0.006
8	19.4471	0.17	0.225	18.5329	0.16	0.221	0.004
9	19.4933	0.21	0.179	18.5815	0.13	0.173	0.006
IP	19.672			18.754			

(a) Data from Reference (12, 13)

Figure Captions

Fig. 1 Absorption spectrum of CO in the photon energy range from 10.1 eV to 14.3 eV covering the range of Rydberg transitions converging on the first ionic state $X^2\Sigma^+$ of CO^+ . The Rydberg transitions $5\sigma \rightarrow n\sigma$ and $\rightarrow n\sigma$ are given on top of the spectrum. Transitions to other excited states are discussed in Ref. 15. In the photon energy range below 12.0 eV the apparent background absorption is due to higher order intensity from the monochromator.

Fig. 2 Term value versus ionization energy correlation lines for corresponding Rydberg states in the isoelectronic molecules BF, CO and N_2 . Circles represent data for the $n\sigma$ (0,0) states while crosses stand for those of $n\pi$.

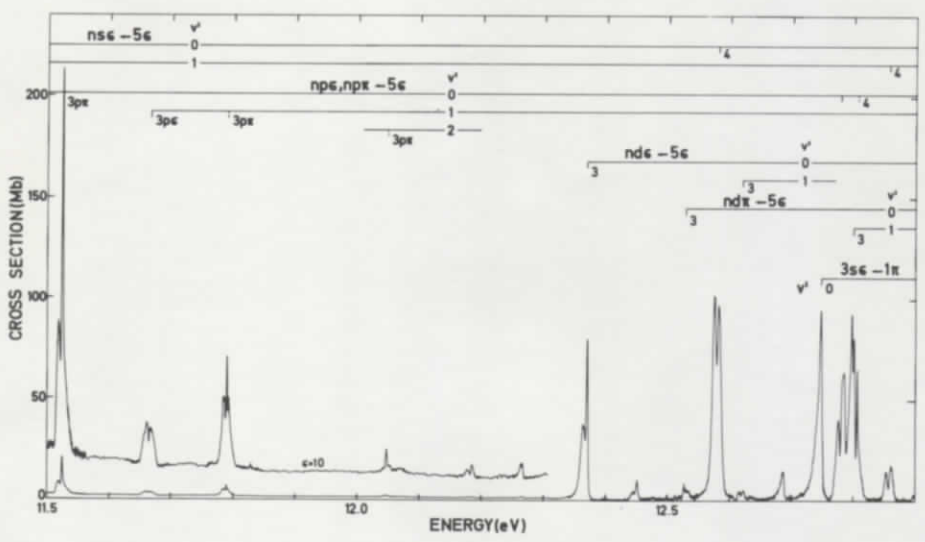
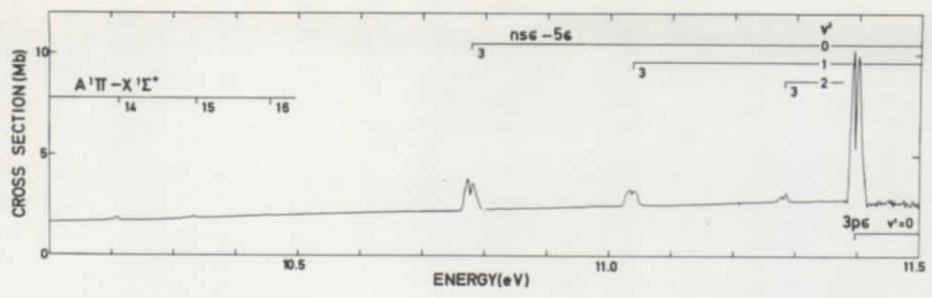


Fig. 1

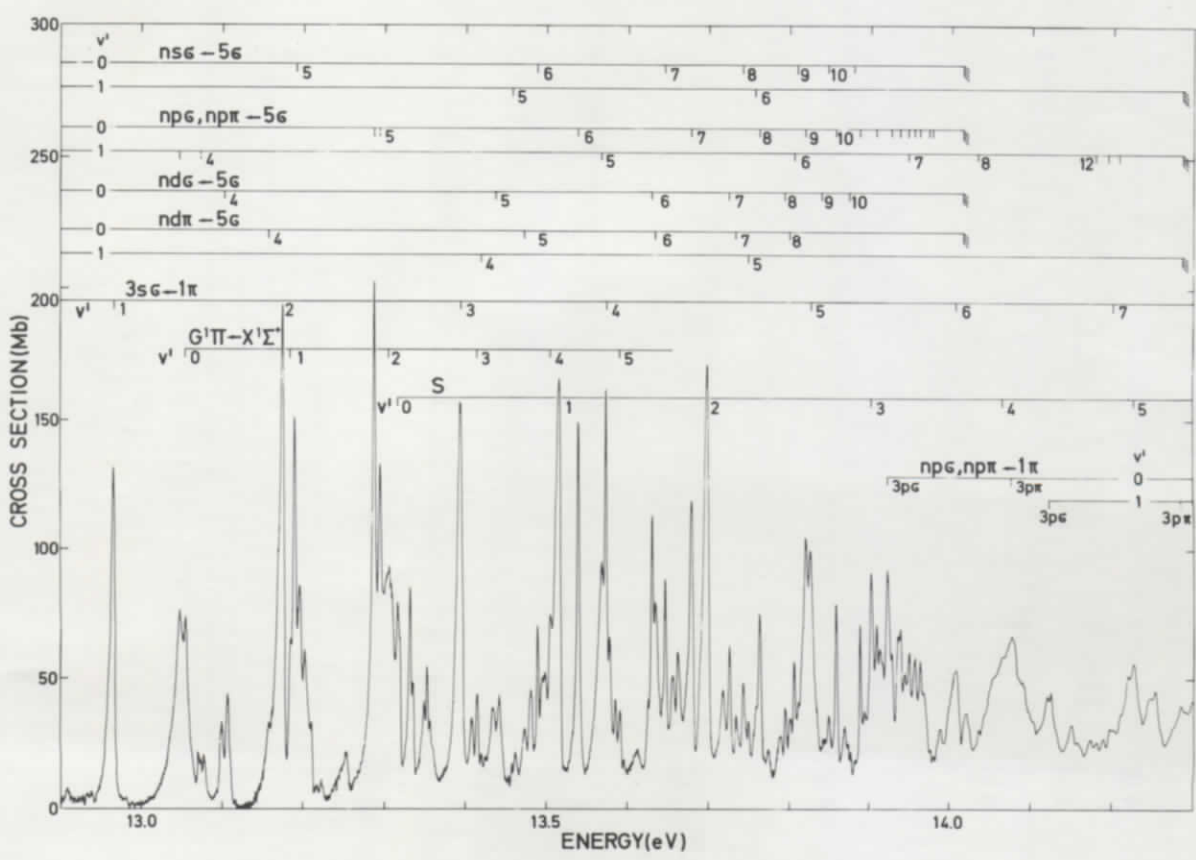


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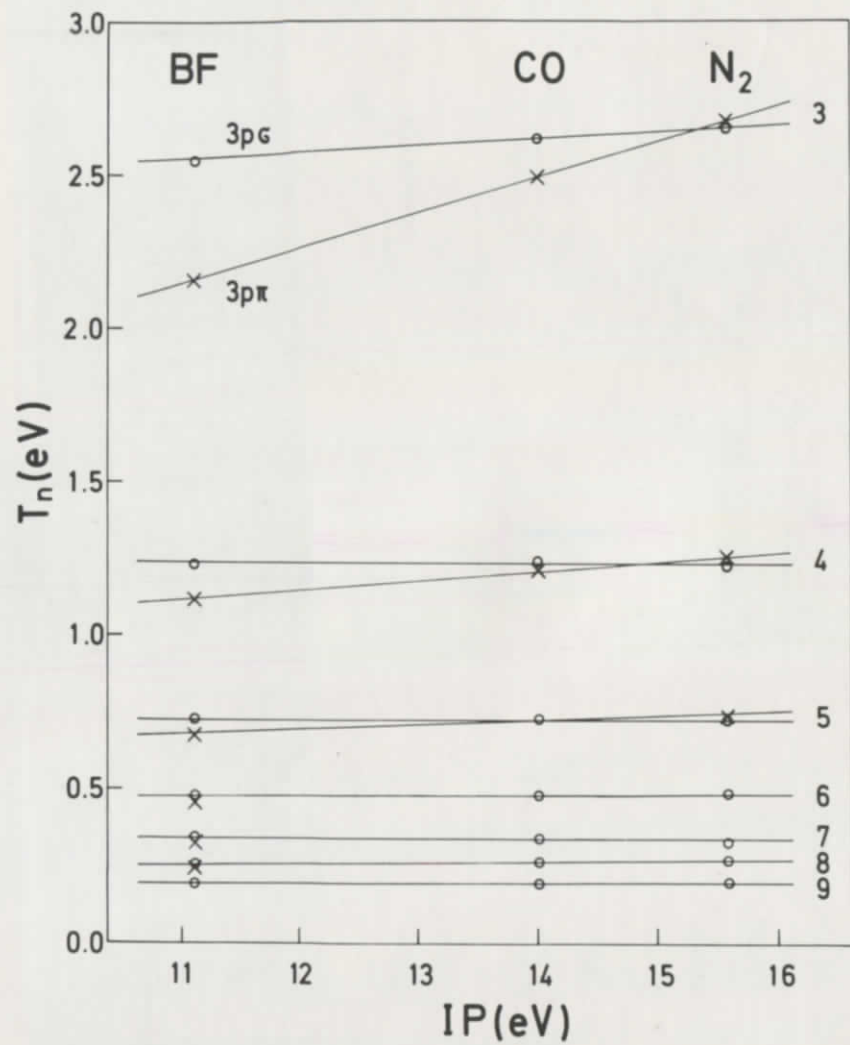


Fig. 2