UVPES and ab Initio Molecular Orbital Studies on the Electron Donor−Acceptor Complexes of Bromine with Methylamines[†]

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The He I photoelectron spectra of bromine, methylamine, and their complex have been obtained, and the spectra show that lone-pair orbital energy of nitrogen in methylamine is stabilized by 1.8 eV and the bromine orbital energies are destabilized by about 0.5 eV due to complexation. Ab initio calculations have been performed on the charge-transfer complexes of Br_2 with ammonia and methyl-, dimethyl-, and trimethylamines at the 3-21G*, 6-311G, and 6-311G* levels and also with effective core potentials. Calculations predict donor and acceptor orbital energy shifts upon complexation, and there is a reasonable agreement between the calculated and experimental results. Complexation energies have been corrected for BSSE. Frequency analysis has confirmed that ammonia and trimethylamine form complexes with C_{3v} symmetry and methylamine and dimethylamine with C_s symmetry. Calculations reveal that the lone-pair orbital of nitrogen in amine and the σ^* orbital of Br_2 are involved in the charge-transfer interaction. LANL1DZ basis seems to be consistent and give a reliable estimate of the complexation energy. The computed complexation energies, orbital energy shifts, and natural bond orbital analysis show that the strength of the complex gradually increases from ammonia to trimethylamine.

1. Introduction

Molecular interactions between closed-shell systems figure prominantly in diverse phenomena, namely, conformational dynamics of biomolecules,[1] conduction in polymers[2] and organic molecular crystals,[3] and the existence of stable ground-state electron donor−acceptor (EDA) bimolecular complexes.[4] As a result of the development of new theoretical approaches and new experimental methods, it has become possible to observe fascinating progress in the study of molecular interactions.

The present study is an experimental and theoretical investigation of the structural features and binding energies of the molecular complexes of Br_2 with amines in the gas phase. The molecular complexes of amines with halogens that fall under the category of charge-transfer complexes were known well before the charge transfer theory was proposed by Mulliken.[5] The charge-transfer complex in the gas phase could be investigated by gas-phase electron diffraction,[6] ultraviolet photoelectron spectroscopy[7] (UVPES), and electron energy loss spectroscopy[8] (EELS). Theoretical methods have also been employed to study them, as they are especially suitable for vapor-phase phenomena. Ab initio quantum chemical methods are increasingly used in obtaining the geometry, binding energy of the complex, and orbital shifts in them. Theoretical investigations can be effectively coupled with gas-phase experimental studies on them to fully characterize the complexes and to reveal the nature of the interactions in them at the orbital level. Under such circumstances, they provide new and valuable insights. Though the EDA complexes of amine−halogens were well-known and as old as the charge-transfer theory is, they have been studied time and again,[9−12] as they are prototype complexes in the realm of intermolecular interactions. The EDA complexes of NH_3 and methylamines with F_2 and Cl_2 have been thoroughly studied both at the SCF and the MP2 levels,[13] while there are only a few reports[14] available in the literature on the ab initio study of Br_2 and I_2 complexes. Perhaps due to the size factor of Br_2 and I_2, they have been less investigated. On the experimental side, UVPES is a powerful tool to obtain the electron states of molecular complexes in the gas phase. This is due to the fact that, even if the amount of charge transfer is less, the donor and acceptor orbitals are shifted by several electronvolts and orbital shifts are directly observable through UVPES. Much the same occurs with the theoretical methods; orbital shifts due to complexation can be accurately calculated. A combination of these two has been tried out here on the prototype complexes—amines with bromine.

Further, UVPES is the method of choice to study molecular complexes involving Cl_2 and Br_2, as their CT bands are shifted to the vacuum UV region and, therefore, are not amenable for conventional UV spectroscopic study. We have already investigated EDA complexes of Br_2 with various donors such as diethyl ether, diethyl sulfide, benzene, etc.,[15,16] through UVPES and ab initio calculations. The EDA complexes of Br_2 with NH_3, methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) have been tried for the first time using UVPES. Among them, the $NH_3\cdots Br_2$ complex is photodissociating due to surface reaction, and therefore, the complex spectra could not be recorded. DMA and TMA form stronger solid complexes with Br_2, and due to this, gas-phase study in these two cases has not been possible. MA, which forms a relatively weak complex with Br_2, is the only member in the series that is amenable for UVPES study. Here we report the first UVPES spectra of the $MA\cdots Br_2$ complex and the ab initio calculations for the complexes of Br_2 with NH_3, MA, DMA, and TMA.

2. Experimental and Computational Details

A home-built ultraviolet photoelectron spectrometer consisting of a He I UV lamp, a 3-mm-diameter collision chamber, and channeltron electron multiplier was employed to determine the

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orbital energies.[17] Differential pumping enabled operation of the He I lamp at 1.5 Torr, a sample pressure of 0.1−0.5 Torr, and maintanence of 5×10^{-5} Torr of pressure in the rest of the spectrometer. The resolution of the spectrometer is 60 meV at 6.06 eV (KE).

Methylamine gas was purified by passing it through KOH and then collected in a glass bulb at 700 Torr. Bromine was taken in a glass ampule and connected to the spectrometer by a variable leak valve. First, the monomer spectra of bromine and methylamine were independently obtained. Samples of the complexes were prepared in a glass vacuum system by cocondensation of the donor and the acceptor in a glass bulb fitted with a teflon valve. The gas line was pumped for a long time to eliminate peaks due to HBr. When the photoelectron spectra of HBr were present, no peaks due to bromine were observed. Only after HBr impurity was removed were the spectra due to the monomers and complex obtained. Initially, the UVPES of only the donor molecule was observed. After excess donor was removed by continuous pumping, the photoelectron spectra of both the monomers and the complex appeared. The spectra were recorded a number of times to establish the peak position.

The calculations were carried out at the single-configuration self-consistent-field (SCF) level of theory. The molecular geometries of the complexes and monomers were fully optimized at the SCF level. All-electron 3-21G*,[18] 6-311G,[19] and 6-311G*[19] basis sets were used. 6-311G specifies the 6-311G basis for first-row atoms and the McLean−Chandler (12s,9p) → (621111,52111) basis for second-row atoms and the Wachters−Hay all-electron basis set for the first transition row, using the scaling factors of Raghavachari and Trucks. Effective core potentials[20] were also used with the DZ basis set for the first-row atoms. Single-point MP2 calculations were carried out at the 6-311G* optimized geometries. The C_{3v} symmetry is assumed for the NH_3 and TMA complexes and C_s symmetry for the MA and DMA complexes. The interaction energies were corrected for basis set superposition error (BSSE) using the Boys and Bernardi counterpoise method.[21] The interaction between the molecules at the orbital level were analyzed by performing natural bond orbital (NBO)[22] calculations on the complexes. The harmonic frequency analysis of the complexes at the SCF level with the 3-21G* and 6-311G basis sets was performed. All calculations were carried out with the GAUSSIAN 92[23] and GAUSSIAN 94[24] series of programs implemented on an IBM RS6000 system.

3. Results and Discussion

UVPES of the Methylamine−Br$_2$ Complex. The He I photoelectron spectra of Br_2, CH_3NH_2, and their complex are shown in Figure 1. Bromine exhibits peaks at 10.55, 10.91, 13.09, and 14.91 eV. The first two peaks are derived from the π_g MO and split due to spin−orbit coupling, while the remaining peaks correspond to π_u and σ_g MOs, respectively. The first ionization energy of methylamine at 9.63 eV is due to the nitrogen lone pair, and features at 13.37, 14.31, and 15.69 eV are due to π_{CH_3}, σ_{CN}, and π_{CH_3}. These values match well with those reported in the literature.[25] The additional features observed in the spectrum of methylamine−Br_2 shown in Figure 1 are due to complex formation. Four prominent peaks at 10.06, 10.44, 11.22, and 12.62 are found. The appearance of monomer as well as complex peaks in the complex spectra shows that the complex exists in equilibrium with the monomers. Ab initio MO calculations have been used in assigning the various peaks observed and to understand the nature of the molecular interactions.

Geometries of the Complexes. The RHF-optimized equilibrium structures of the complexes are presented in Figure 2.

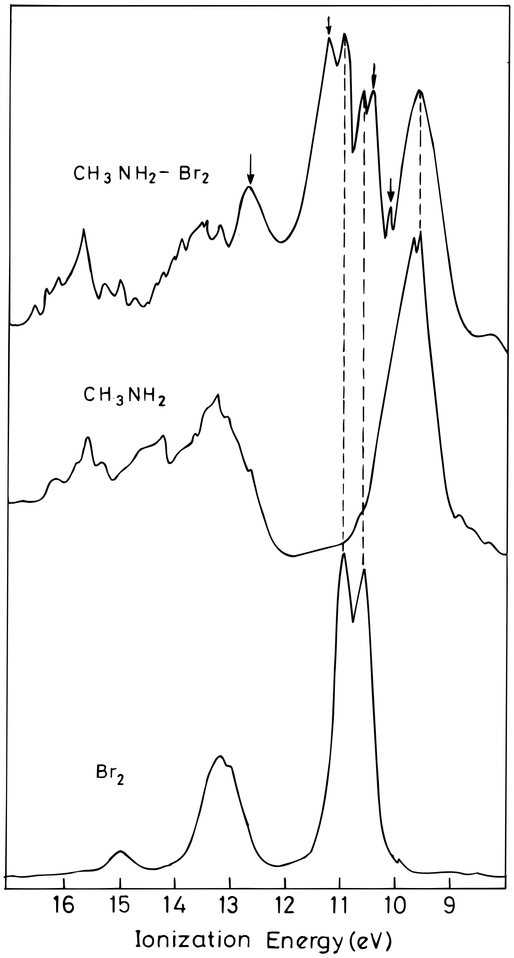

Figure 1. He I photoelectron spectra of Br_2, methylamine, and the methylamine−Br_2 complex. Features due to the complex are marked by arrows.

For all the complexes, the harmonic vibrational frequencies are all real, and it is confirmed therefore that the obtained geometries are true minimum geometries. The N···Br distances in all the complexes are significantly shorter than the sum of the van der Waals radii of N and Br (3.45 Å), and the Br−Br distances increased characteristic of complex formation. The geometries of NH_3 and methylamines are only slightly changed on complexation. Notable changes are observed in the N···Br and the Br−Br distances in complexes and also in the angle around the nitrogen atoms, and they are summarized in Table 1. With the increase in the number of methyl groups, the donor strength of the amine is expected to increase; in turn, the CT interaction should increase and the complex becomes stronger. This is well reflected in the calculated N···Br and Br−Br distances, the former gradually decreasing and the latter increasing from ammonia to trimethylamine. Further, as the lone pair of the nitrogen atom of the amines are donated on complexation, the geometry around the nitrogen atoms changes from pyramidal to tetrahedral. This can be noted from a comparison of the angle around the nitrogen atom in the simple amines and the complexed amines. One can also note from these values that the tendency toward more tetrahedral geometry around nitrogen is increased with the extent of donation of the lone pair to Br_2. Calculations performed with different basis sets show similar trends in the structural parameters of the complexes except for the 6-311G* basis. However, 6-311G* Br−Br distance for the simple bromine molecule agrees well with the reported experimental value (2.29 Å).[26]

The gas-phase electron diffraction study of the TMA···Br_2

TABLE 1: Selected Structural Parameters for the Amine−Br_2 Complexes

parameter	basis		Br_2	$NH_3\cdots Br_2$	$MA\cdots Br_2$	$DMA\cdots Br_2$	$TMA\cdots Br_2$
R_{N-Br}, Å	3-21G*			2.611	2.555	2.518	2.487
	6-311G			2.597	2.516	2.467	2.457
	6-311G*			2.810	2.775	2.771	2.803
	LANL1DZ			2.621	2.549	2.502	2.479
R_{Br-Br}, Å	3-21G*		2.270	2.307	2.313	2.320	2.323
	6-311G		2.392	2.449	2.467	2.481	2.485
	6-311G*		2.289	2.311	2.315	2.315	2.313
	LANL1DZ		2.462	2.515	2.531	2.543	2.551
angle around N, deg	3-21G*	M[a]		337.2	338.5	339.6	339.1
		C		334.9	336.1	336.0	336.9
	6-311G	M		343.4	342.3	341.9	340.8
		C		337.6	337.4	337.2	336.9
	6-311G*	M		322.3	328.1	332.6	335.5
		C		323.4	328.7	332.3	334.7
	LANL1DZ	M		348.9	345.7	343.6	341.0
		C		339.1	338.7	337.8	336.8

[a] M and C denote the monomer and complex, respectively.

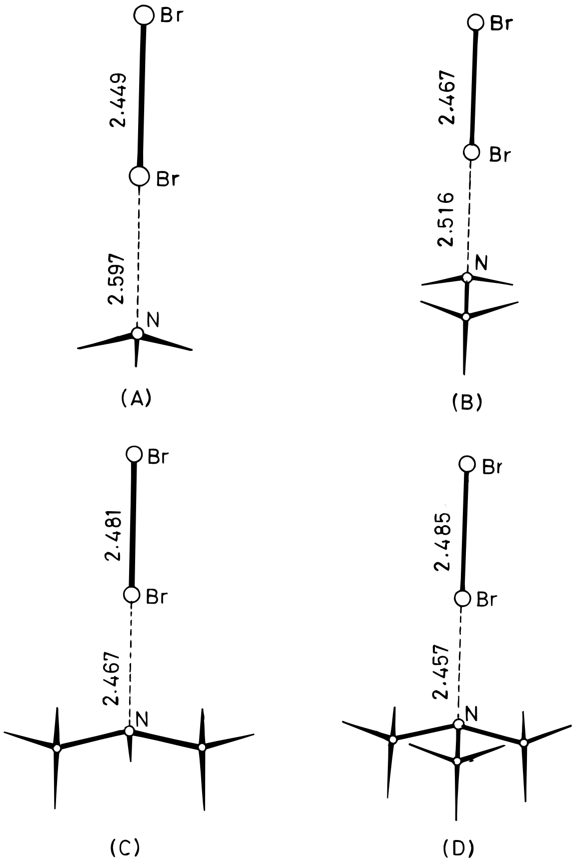

Figure 2. Optimized geometries of the amine−Br_2 complexes: (A) ammonia···Br_2; (B) monomethylamine···Br_2; (C) dimethylamine···Br_2; (D) trimethylamine···Br_2 (bond lengths (in Å) given are calculated at the 6-311G level).

complex has been reported by Shibata and Iwata.[6] They have reported that TMA···Br_2 has a different geometry compared to all other amine complexes with I_2, ICl,[27] etc., and according to them, the N−Br−Br bond is not linear. They could not find any change in the Br−Br bond length due to complexation. This is highly unlikely and contrary to the usual trends on geometric changes on complexation in amine−halogen[27] complexes. It may be noted that TMA forms a solid complex with Br_2 in our trials and PE spectra could not be recorded. Ab initio calculations with off-axis alignment of Br_2 with TMA showed that it did not converge to a stable geometry. In view of the above basic differences, it may not be worthwile to compare our results with the reported electron diffraction data.

Energetics. The formation energies ΔE_b of the complexes of Br_2 with ammonia and methylamines computed at different levels of calculations are given in Table 2. The basis set superposition corrections are quite large for the 3-21G* basis set, and the corrected formation energies ΔE_b^{cp} are also given in the same table. The computed complexation energies are highly dependent on the level of calculations. The 3-21G* basis set overestimates the complexation energies. But after BSSE correction, they give reasonable values. The complexation energies obtained from the 6-311G, 6-311G*, and LANL1DZ calculations are almost near to the BSSE-corrected complexation energies of the 3-21G* basis set. The inclusion of electron correlation shoots up the binding energy. BSSE correction is found to be minimal when the level of the basis set is increased. Overall, the LANL1DZ results seem to be reasonable. The electron-donating power of the nitrogen atom increases when the number of methyl groups are increased. The complexation energy of the amine−Br_2 complexes should therefore increase in the order NH_3 < MA < DMA < TMA. This trend can be observed almost with all basis sets. In the case of the 3-21G* calculations, though it showed the expected ordering before BSSE correction, the trend is totally reversed once BSSE corrections are included. The expected ordering is also not observed in the 6-311G* basis, but inclusion of electron correlation again reproduce the correct ordering to some extent.

EDA complexes involving diethyl ether and diethyl sulfide with Br_2 have been examined earlier.[15] As expected, the amine complexes are stronger compared to the ether and sulfide complexes. This can be noted from the formation energies of these complexes with those of diethyl ether and sulfide.

Analysis of Interactions. Electronic interaction between a donor and acceptor during complexation results in significant changes in donor as well as acceptor orbital energies and occupancies of frontier molecular orbitals. Consequently, charges on atoms, especially those involved directly in complexation, and dipole moments are increased. Such changes are normally proportionate to the strength of the complexes, and therefore, the magnitude of the change in them is taken as a measure of the strength of interaction between a donor and acceptor. The dipole moments of the complexes (Table 3) increase by increasing the number of methyl groups in the donor. NBO analysis gives more information on the nature and magnitude of the interaction at orbital level. The results obtained from NBO analysis are summarized in Table 4. The net charge transfer to the Br_2 unit from the amine is increased from NH_3 to TMA. The orbital occupancy values clearly indicate that the interaction mainly involves the nitrogen lone

TABLE 2: Calculated Complexation Energies (ΔE_b) and the Counterpoise Corrected Complexation Energies (ΔE_b^{cp}) of the Amine−Br_2 Complexes (in kcal/mol)

parameter	basis	$NH_3\cdots Br_2$	$MA\cdots Br_2$	$DMA\cdots Br_2$	$TMA\cdots Br_2$
ΔE_b	3-21G*	10.60	10.99	11.12	11.13
ΔE_b^{cp}		6.19	5.97	5.46	4.79
ΔE_b	6-311G	6.36	7.18	7.51	7.29
ΔE_b^{cp}		5.34	5.82	5.91	5.56
ΔE_b	6-311G*	5.50	5.71	5.49	4.95
ΔE_b^{cp}		4.91	4.88	4.48	3.79
ΔE_b	MP2/6-311G*//6-311G*	8.91	10.43	11.41	11.77
ΔE_b^{cp}		7.42	8.43	9.03	9.07
ΔE_b	LANL1DZ	6.34	7.49	8.18	8.46
ΔE_b^{cp}		5.57	6.46	6.96	7.03

TABLE 3: Dipole Moments (in D) of the Amine−Br_2 Complexes

complex	3-21G*	6-311G	LANL1DZ
$NH_3\cdots Br_2$	4.830	5.389	5.377
$MA\cdots Br_2$	4.922	6.085	6.058
$DMA\cdots Br_2$	4.939	6.511	6.504
$TMA\cdots Br_2$	4.913	6.521	6.706

TABLE 4: Natural Bond Orbital Analysis for Geometries Optimized at the 6-311G Level

	$NH_3\cdots Br_2$	$MA\cdots Br_2$	$DMA\cdots Br_2$	$TMA\cdots Br_2$
charge, au				
Br_2	−0.094	−0.121	−0.140	−0.144
occupancy, au				
σ_u	0.0961	0.1237	0.1426	0.1464
n_N	1.9012	1.8544	1.8149	1.7895
$E^{(2)}$, kcal/mol				
n_N, σ_u	33.01	41.37	46.19	44.80

TABLE 5: Vertical Ionization Energies, Calculated Orbital Energies, and Assignments of Bromine, Methylamine, and the Complex

	$-\epsilon$, eV				
molecule	3-21G*	6-311G	6-311G*	*I*, eV	assignment
Br_2	10.70	11.44	11.10	10.55, 10.91	π_g
	13.49	13.64	13.76	13.09	π_u
	14.35	13.98	14.61	14.91	σ_g
MA	9.88	10.03	10.49	9.64	n_N
	14.06	14.19	14.10	13.31	π_{CH_3}
	15.02	15.36	15.18	14.37	σ_{CN}
	16.08	16.26	16.42	15.62	π_{CH_3}
MA− Br_2	9.78	10.41	10.42	10.06, 10.44	π_g
	10.52	10.45	11.00	11.22	n_N
	12.37	12.58	12.98	12.62	π_u

TABLE 6: Energies of Selected Molecular Orbitals of the Monomers and Complexes (in au)

molecule	orbital	3-21G*	6-311G	LANL1DZ
Br_2	π_g	−0.3934	−0.4207	−0.4219
	π_u	−0.4958	−0.5015	−0.4948
	σ^*	0.0282	−0.0385	−0.0538
NH_3	n_N	−0.3889	−0.3989	−0.3947
$NH_3\cdots Br_2$	n_N	−0.4073	−0.4054	−0.3994
	π_g	−0.3598	−0.3879	−0.3864
	π_u	−0.4568	−0.4666	−0.4594
	σ^*	0.0812	0.0081	−0.0051
MA	n_N	−0.3632	−0.3688	−0.3562
$MA\cdots Br^2$	n_N	−0.3868	−0.3843	−0.3787
	π_g	−0.3584	−0.3827	−0.3810
	π_u	−0.4546	−0.4626	−0.4553
	σ^*	0.0833	0.0123	−0.0002
DMA	n_N	−0.3455	−0.3497	−0.3465
$DMA\cdots Br_2$	n_N	−0.3714	−0.3690	−0.3646
	π_g	−0.3575	−0.3794	−0.3766
	π_u	−0.4530	−0.4598	−0.4523
	σ^*	0.0845	0.0149	0.0034
TMA	n_N	−0.3336	−0.3372	−0.3347
$TMA\cdots Br_2$	n_N	−0.3596	−0.3592	−0.3549
	π_g	−0.3568	−0.3782	−0.3741
	π_u	−0.4519	−0.4587	−0.4506
	σ^*	0.0854	0.0152	0.0049

pair (n_N) in amines and the σ^* orbital in Br_2. The strength of the complexes can be predicted well from the orbital occupancy values. The second-order perturbation analysis of the orbitals further substantiates the above information. The largest stabilization interaction in all the complexes corresponds to the n_N and σ^* (Br−Br) orbitals, and the stabilization energy increases from NH_3 to TMA.

Due to these kinds of electronic interactions between the donor and acceptor molecules, one can also observe the changes in the orbital energies of the interacting molecules. The observed photoelectron spectra clearly indicate the changes in the orbital levels due to complex formation. The PE spectra have been assigned using ab initio orbital energies in conjunction with Koopmans' theorem.[28] The computed orbital energies of Br_2 and MA are generally consistent with the observed vertical ionization energies (Table 5) and follow the expected sequence of orbital ordering. With this order while assigning the peaks of the $MA\cdots Br_2$ complex, the first two features at 10.06 and 10.44 eV are attributable to the split π_g orbitals of the Br_2 unit due to the spin-orbit splitting. The peak at 11.22 eV is due to the ionization from the nitrogen lone pair of MA. The peak at 12.62 eV would then correspond to ionization from the π_u orbital of Br_2. In effect, the nitrogen lone pair is shifted by 1.8 eV to a higher binding energy and Br_2 orbitals are shifted to lower binding energies of about 0.5 eV as a result of complex formation. The same trends are noted in the computed orbital energies at the different levels employed.

The shift in the ionization energy for the lone pair on nitrogen in this complex is large compared to the shift for oxygen and sulfur lone pairs in the complexes of Br_2 with diethyl ether and diethyl sulfide (0.2 and 0.3 eV, respectively).[15] A similar trend has been already observed for the complexes of SO_2 with the same set of donors[29] and is clearly in accordance with the strength of the donors employed.

It is worthwhile to mention here that Utsunomia and co-workers[30] have studied the EDA complexes of Br_2 with *N*,*N*-diethylmethylamine (DEMA), triethylamine (TEA), tri-*n*-propylamine (TPA), and tri-*n*-butylamine (TBA) through UVPES measurements. While their monomer spectra are quite clear, the complex spectra show some unusual features. For instance, the sharp peak appearing at 11.7 eV in all the complex spectra must be due to π_g of Br from HBr impurity. They have also noted the presence of water in the mixture. In the presence of water, HBr forms. Further, there are no peaks corresponding to the nitrogen lone pair from unreacted amine.

The orbital energies for all the complexes and monomers computed with different basis sets are presented in Table 6. It is clear that, on complexation, the donor orbitals are stabilized while those of the acceptor are destabilized. This is due to charge transfer from the donor orbital (HOMO) to the LUMO

TABLE 7: Intermolecular and Halogen Stretching Vibrations of the Amine−Bromine Complexes (in cm^{-1})

	$\nu_{\mathrm{Br-Br}}$		$\nu_{\mathrm{N-Br}}$	
molecule	3-21G*	6-311G	3-21G*	6-311G
Br_2	370	310		
$NH_3\cdots Br_2$	335	268	182	162
$MA\cdots Br_2$	328	261	139	138
$DMA\cdots Br_2$	330	241	125	127
$TMA\cdots Br_2$	312	234	113	116

of the acceptor. In this case, the nitrogen lone-pair orbital forms the HOMO and the σ^* of Br_2 forms the LUMO. The magnitude of the shift in the orbital energies is generally proportional to the strength of the charge-transfer interaction, and this can be observed from the computed values presented in Table 6.

On complexation, an electron is accepted into the σ^* orbital of Br_2, and therefore, the Br−Br bond is weakened. This shows up in lengthening of this bond and a corresponding lowering of the harmonic frequency of the Br−Br stretching mode. With the extent of charge transfer increasing from NH_3 to TMA, the frequency of the Br−Br stretching mode is gradually lowered. This can be seen from Table 7, which presents the harmonic frequencies of the intramolecular Br−Br stretching and the intermolecular N⋯Br stretching computed at the 3-21G* and 6-311G levels. When the amines and Br_2 form complexes, the N⋯Br bond starts forming and the strength of this bond increases with increasing the donor strength. Therefore, naturally, the harmonic frequency corresponding to the stretching of the bond is expected to increase from NH_3 to TMA. But on the contrary, this is also found to be decreasing in the same order. A similar trend is reported for the amine−Cl_2 complexes.[12] This may be due to the different values of reduced mass in each case and coupling of various vibrational modes of the complex with this stretching mode.

4. Conclusions

The photoelectron spectra of methylamine, bromine, and their complex clearly show a characteristic picture of a weak n−σ^* interaction in the complex. Ab initio calculations show that NH_3, MA, DMA, and TMA form relatively stronger charge-transfer complexes with Br_2, and in the complex, an electron from the lone-pair orbital of the amine is donated into the σ^* orbital of the Br_2 molecule. The strength of the complex increases from NH_3 to TMA. The calculations with basis sets 6-311G, 6-311G*, and LANL1DZ give reasonable binding energies compared to the 3-21G* basis set, and the LANL1DZ basis reproduces the correct basicity scale. The inclusion of electron correlation increases the binding energy of the complex. The strength of the interaction in the complexes is reflected in the optimized structures, complexation energies, magnitude of charge transfer, orbital occupancy values, vibrational frequencies, and orbital energy shifts. A reasonable agreement between the computed orbital energies and UVPES values has been seen in the case of the $MA\cdots Br_2$ complex. This confirmed that the calculated results are in the right direction and of the right magnitude and has enabled us in obtaining valid conclusions for other complexes where calculated results alone are available.

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