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The Mechanism of the Collision-Induced Enhancement of the $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ and $b^1\Sigma_g^+ \rightarrow a^1\Delta_g$ Radiative Transitions of O_2[†]

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Large sets of literature data on the enhancement of the O_2 emissions $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ in solution and $b^1\Sigma_g^+ \rightarrow a^1\Delta_g$ in the gas phase have been analyzed. Second-order rate constants have been interpreted with respect to molecular parameters such as collision frequency, molecular size, and molecular polarizability of the collider. It is shown that the transition moments of both collision-induced radiative transitions are directly proportional to the molecular polarizability of the collider, if the effects of collider size and collision frequency are removed. A transient shift of electron density from the collider MOs into the $\pi_{g,x}$ and $\pi_{g,y}$ molecular orbitals of O_2 occurs, which induces electric dipole character into the b → a transition. Because of the strong spin-orbit coupling of O_2, the a → X transition profits proportionally from the enhancement of the b → a transition by intensity borrowing.

Introduction

Two excited singlet states, $b^1\Sigma_g^+$ and $a^1\Delta_g$, lie closely above the $X^3\Sigma_g^-$ triplet ground state of O_2.[1] The transitions between these states are strictly forbidden for the isolated O_2 molecule by the selection rules for electric dipole radiation.[1−3] Intermolecular interactions lead to a strong enhancement of the b → a and a → X emissions in the gas and in the condensed phase.[4−12] Although some data have recently also been published on the b → a and b ← a radiative transitions in solution,[9−12] by far the most liquid phase data have been collected for the a → X phosphorescence, occuring at about 1275 nm.[13−25] The corresponding first-order rate constant k_{a-X} is by three to four orders of magnitude larger in solution than in the diluted gas phase and varies from about 0.2 (H_2O) to 3 s^{-1} (CH_2I_2). The interpretation of this extraordinary solvent effect on a radiative rate constant is still a matter of controversy. Ogilby et al.[13,16] found rather smooth correlations of k_{a-X} with the solvent refractive index n or functions of n, e.g., the bulk polarizability $P = (n^2 - 1)/(n^2 + 2)$. They concluded that dispersion interactions are the main reason for the solvent dependence of k_{a-X}. It was speculated that the solvent dependence of k_{a-X} could be interpreted on the basis of a Kirkwood/Onsager reaction field model, considering the solvent as a homogeneous and isotropic dielectric medium.[16] Ref. 17 found a roughly linear correlation of $\log(k_{a-X}/n^2)$ with the ionization potential IP of the solvent molecules. He assumed that charge-transfer (CT) interactions lift the forbiddeness of the a → X radiative transition.[17] We finally arrived at a different perspective of the solvent effect on k_{a-X}, which explicitely considers the role of bimolecular collisions of $O_2(^1\Delta_g)$ with solvent molecules. We found that second-order rate constants k^c_{a-X} of the radiative transition are almost proportional to the square of the molar refraction R of the collider, qualitatively indicating proportionality of the collision-induced transition moment with the collider's molecular polarizability.[9] Despite these results, the bimolecular nature of the process leading to the enhancement of the a → X radiative transition is still presently ignored in the analysis of k_{a-X} data.[24−26]

Bilski et al.[24] assumed some specific interactions to explain the anomalous dependence of k_{a-X} on the bulk polarizability P in mixtures of D_2O and acetonitrile instead of evaluating their data quantitatively on the basis of second-order rate constants k^c_{a-X}.[12] Just recently, two further publications appeared, discussing the possible effect of CT interactions on the a → X radiative transition in solution on a large data basis.[25,26] However, these investigations also disregarded the bimolecular nature of the perturbation process. Darmayan presented new data of k_{a-X} for 17 solvents.[25] Adding literature data he now used pseudo-first-order rate constants k_{a-X} for 63 pure solvents for interpretation. He divided values of k_{a-X} by the energy of dispersion interaction of $O_2(^1\Delta_g)$ with the respective solvent molecules and correlated the logarithms of these ratios with the solvent molecule IP. On the basis of this analysis, Darmanyan proposed again CT interactions as the main factor in the removal of the forbiddeness of the a → X radiative transition.[25] Poulsen et al.[26] also interpreted pseudo-first-order rate constants and compared correlations of k_{a-X}/n^2 vs the bulk parameter n with correlations of k_{a-X}/n^2 vs the molecular parameter IP. Irrespective of whether they used the 29 values of k_{a-X} of ref 16 or an extended data set of 56 values of k_{a-X}, which includes most of the new data of Darmanyan, they demonstrated the superiority of the correlation of k_{a-X}/n^2 vs n. It was concluded that instead of CT interactions the electronic response of the solvent would be a key parameter in the effect of solvent on the a → X transition probability.[26]

However, the actual mechanism of the perturbation process leading to the solvent dependence of k_{a-X} can only be revealed if the bimolecular nature of the radiative transition in solution explicitly is taken into account. Second-order rate constants $k^c_{a-X} = k_{a-X}/[M]$ are obtained from k_{a-X} values of pure solvents M and the corresponding molarities [M]. In a very recent publication we demonstrated that the anomalous dependence of k_{a-X} on P in the solvent mixtures H_2O/acetone and $CH_3OH/CHCl_3$

[†] Dedicated to Professor H.-D. Brauer on the occasion of his 65th birthday.

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can easily and quantitatively be interpreted on the basis of the k^c_{a-X} data of the mixture components.[12] Furthermore, we analyzed for 13 solvents the dependence of k^c_{a-X} on the molecular polarizability of the collider, which is expressed in the range of optical frequencies by the molar refraction $R = 1000\ P/[M]$. We discovered that the molecular size of the collider strongly controls the effect of R on k^c_{a-X}. Considering the effects of refractive index and collision frequency and using a model for the size-dependence, we demonstrated that a direct proportionality of the transition moment of the emission with the collider's molecular polarizability exists.[12]

These results rest on the analysis of only a rather small data basis. Thus, still some doubts about our conclusions could remain. However, with the recent new data of us[12] and Darmanyan[25] and the data compilations of Darmanyan[25] and Ogilby et al.[16,26] there is now indeed a large body of experimental data that the scientific community can agree upon. We will use this extended and rather reliable data set for a brief general analysis of the enhancement of the a → X radiative transition in solution, investigating the molecular events of the perturbation process. Hereby, it will be seen whether our previous conclusions concerning the mechanism of the solvent perturbation of the a → X transition are confirmed and deserve general acceptance.

Data

Table 1 lists the data basis for the a → X emission. The 12 k_{a-X} values determined recently by us[12] are complemented by the 21 nonoverlapping k_{a-X} data of the compilation of ref 16. Since for CH_2I_2 $k_{a-X} = 4.08\ s^{-1}$ of ref 16 differs distinctly from the new value of $2.0\ s^{-1}$ of Darmanyan,[25] we replace both values by the average $k_{a-X} = 3.04\ s^{-1}$. Furthermore, we add the remaining 17 new k_{a-X} values of Darmanyan[25] and with exception of the value for freon 113, which was measured by a rather uncertain stationary technique without sufficient control of the $O_2(^1\Delta_g)$ lifetime, the remaining eight nonoverlapping k_{a-X} data of our previous work[14] as well as the six nonoverlapping rate constants of Darmanyan's recent data compilation to Table 1.[25] Thus, we can now analyze a large data base resting on altogether 64 solvents. For means of comparison we also investigate the influence of the molecular polarizability of the collider on the bimolecular rate constant of the collision-induced b → a transition. The data, which all have been determined by Fink et al.[4] in the diluted gas phase, are listed in Table 2.

Discussion

Intensity Borrowing. According to Minaev,[28,29] the MOs $\pi_{g,x}$ and $\pi_{g,y}$ of O_2 acquire to a different degree dipole moments M_x and M_y in collision complexes because of an admixture of the collider's MOs. Hereby, electric dipole character is induced into the b → a transition. Quantitatively, the transition moment of the collision-induced b → a transition should be determined by the difference of the induced dipole moments: $\mathbf{M}_{b-a} = 0.5(M_x - M_y)$.[29] Since the spin-orbit coupling (SOC) of oxygen is strong, the $X^3\Sigma_g^-$ ground state of O_2 has some $b^1\Sigma_g^+$ character. The admixture coefficient is given by $C = \zeta/E_\Sigma$, where $\zeta = 176\ cm^{-1}$ and $E_\Sigma = 13121\ cm^{-1}$ are the SOC constant of O_2 and the $b_1\Sigma_g^+$ excitation energy, respectively.[2,28,29] Because of the mixing of the $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ states, the a → X transition profits from the collision-induced enhancement of the b → a transition by intensity borrowing. Minaev obtained for the corresponding transition moment $\mathbf{M}_{a-X} = -C\mathbf{M}_{b-a}$, leading with $E_\Delta = 7882\ cm^{-1}$ to eq 1. Thus, in the simple form of the theory the ratio of the rate constants k_{a-X} and k_{b-a} of a given collider should in principle be determined by the SOC constant of O_2 as $k_{a-x}/k_{b-a} = 6.1 \times 10^{-4}$.[29]

$$\frac{k_{a-X}}{k_{b-a}} = \frac{C^2 E_\Delta^3}{(E_\Sigma - E_\Delta)^3} \qquad (1)$$

We recently obtained from liquid phase measurements of the a → X and b → a radiative transitions in CCl_4, C_2Cl_4, and C_4Cl_6 moderately varying ratios k_{a-X}/k_{b-a} with an average value of $k_{a-X}/k_{b-a} = 6 \times 10^{-4}$.[12] Although we did not find the constant ratio expected from eq 1, it is still surprising how successfully the magnitude of the ratio k_{a-X}/k_{b-a} is predicted by the simple theory. These results confirm Minaev's basic idea that the rate constant of the a → X transition borrows intensity from the collision-induced radiative processes b → a via SOC.[9,12]

Mechanism of the Collision-Induced Enhancement of the a → X and b → a Radiative Transitions. The solvent dependence of the second-order rate constants k^c_{a-X} is strong. The data of Table 1 vary by a factor of about 65 from 0.0038 (D_2O) to 0.25 $M^{-1}\ s^{-1}$ (CH_2I_2). The question arises, which parameters determine this large variation of k^c_{a-X}. Starting from the fundamental concept of Minaev, whereafter the admixture of electron density into the $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 leads finally to the enhancement of the a → X transition by intensity borrowing, we expected that this asymmetrical transient charge shift should depend on the molecular polarizability or molar refraction R of the colliding molecule.[9] We calculated second-order rate constants k^c_{a-X} from values of k_{a-X} determined earlier by us for 27 solvents.[14]

A plot of $\log(k^c_{a-X})$ vs $\log(R)$ of all data resulted in a roughly linear correlation with slope $s = 1.71 \pm 0.08$. Thus, we found for the first time the strong dependence of k^c_{a-X} on R.[9] In our most recent investigation of a smaller but more accurate data set of 13 solvents we discovered that a graduation of the dependence of k^c_{a-X} on R according to the collider size exists.[12] Colliders with small van der Waals volumes V_{vdW} enhance the a → X transition distinctly stronger than large colliders, if they have similar molecular polarizabilities.

Figure 1 presents the data of Table 1 in a double-logarithmic plot of $\log(k^c_{a-X})$ vs $\log(R)$. A strong correlation between both quantities exists. The only value which does not fit into the general correlation is the value of nitropropane, which will be ignored in the further discussion. A linear least-squares fit to all other data results in a straight line with slope 1.85 ± 0.07 (not shown).

Figure 1 shows impressively that the graduation of the effect of the molecular polarizability on k^c_{a-X} according to the collider size is also observed with the large data basis. The straight line with slope 2.52 ± 0.17 is the linear least-squares fit of the data for the medium size colliders with values of V_{vdW} between 38.6 and 65.5 mL mol^{-1}. The straight line divides the data. The values of $\log(k^c_{a-X})$ of the small colliders ($V_{vdW} \leq 34.7$ mL mol^{-1}) are all above the straight line. The values of the large colliders ($V_{vdW} \geq 67.2$ mL mol^{-1}) are below. Thus, our previous finding is confirmed that for a given molar refraction small colliders are more efficient in the enhancement of the a → X transition.

This remarkable size effect can be understood, if the molecular mechanism of the collision-induced transition is considered. Only those MOs of the colliding molecule, which overlap with the $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 in the collision, can strongly contribute to the enhancement of the a → X radiative transition by a transient shift of electron density. Those MOs, which are farther away from O_2 in the collision complex, of

TABLE 1: Solvent Effect on the a → X Radiative Transition of O_2

solvent	k_{a-X}, s^{-1}	k^c_{a-X}, s^{-1} M^{-1}	n	R, mL mol^{-1}	V_{vdW}[a], mL mol^{-1}
water	0.209[b]	0.0038	1.333	3.71	11.5
water-*d*2	0.206[b]	0.0038	1.338	3.67	11.5
methanol	0.390[b]	0.0159	1.329	8.29	21.7
carbon disulfide	3.14[b]	0.189	1.627	21.3	31.2
1,1,1-trifluoroethanol	0.331[b]	0.0241	1.290	13.2	38.8
acetone	0.543[b]	0.040	1.359	16.2	39.0
chloroform	0.962[b]	0.077	1.448	21.5	41.8
benzene	1.50[b]	0.133	1.501	26.2	48.4
carbon tetrachloride	1.17[b]	0.113	1.460	26.4	49.8
tetrachloroethylene	1.89[b]	0.193	1.506	30.3	56.5
iodobenzene	2.61[b]	0.291	1.619	39.1	65.0
perchlorobutadiene	1.85[b]	0.290	1.555	50.3	90.1
acetonitrile	0.45[c]	0.0234	1.344	11.0	28.4
ethanol-*d*	0.35[c]	0.0203	1.361	13.0	31.9
dichloromethane	0.75[c]	0.048	1.424	16.4	34.7
2-propanol	0.47[c]	0.036	1.377	17.6	42.2
tetrahydrofurane	0.62[c]	0.050	1.407	20.0	45.0
1,4-dioxane	0.56[c]	0.047	1.422	21.7	49.6
diiodomethane	3.04[d]	0.245	1.743	32.6	50.9
fluorobenzene	1.28[c]	0.120	1.465	26.0	51.6
1-iodopropane	1.44[c]	0.140	1.504	28.9	53.3
chlorobenzene	1.68[c]	0.171	1.524	31.2	57.8
toluene	1.44[c]	0.153	1.496	31.0	59.5
cyclohexane	0.66[c]	0.071	1.426	27.7	60.2
benzonitrile	1.80[c]	0.184	1.528	31.4	60.5
bromobenzene	1.97[c]	0.206	1.560	33.9	61.0
trifluorotoluene	1.14[c]	0.139	1.415	30.5	67.2
1,3-dibromobenzene	2.72[c]	0.328	1.608	41.8	73.6
n-heptane	0.66[c]	0.097	1.387	34.5	78.5
1-methylnaphthalene	2.96[c]	0.420	1.616	49.6	85.1
1-bromonaphthalene	3.11[c]	0.432	1.658	51.2	86.6
2-ethylnaphthalene	2.03[c]	0.319	1.598	53.7	95.3
diphenyl sulfide	2.66[c]	0.442	1.633	59.5	102.5
formic acid	0.25[e]	0.0094	1.370	8.54	22.1
dibromomethane	0.80[e]	0.056	1.541	22.1	39.4
propionic acid	0.79[e]	0.059	1.386	17.5	42.6
1,2-dichloroethane	0.75[e]	0.059	1.444	20.9	43.8
2-nitropropane	0.19[e]	0.017	1.394	21.5	50.9
acetic anhydride	0.53[e]	0.050	1.390	22.4	54.4
n-pentane	0.47[e]	0.054	1.358	25.3	58.0
toluene-*d*8	1.47[e]	0.156	1.493	30.9	59.5
anisole	1.80[e]	0.196	1.516	32.8	64.7
n-hexane	0.60[e]	0.078	1.375	29.9	68.3
p-xylene	1.70[e]	0.208	1.495	35.8	70.7
p-chloroanisole	2.20[e]	0.270	1.535	38.1	74.2
p-bromoanisole	1.90[e]	0.238	1.564	40.7	77.3
1,3-dimethoxybenzene	1.90[e]	0.249	1.524	40.1	81.1
1,2,4-trimethylbenzene	2.00[e]	0.270	1.504	40.0	81.8
mesitylene	1.72[e]	0.239	1.499	40.8	81.8
diphenyl ether	2.00[e]	0.317	1.579	52.7	94.9
benzene-*d*6	1.335[f]	0.118	1.498	26.0	48.4
1,2-dibromotetrafluoroethane	1.395[f]	0.168	1.400	29.3	59.9
bromobenzene-*d*5	2.07[f]	0.218	1.557	33.9	61.0
perfluorobenzene	0.51[f]	0.059	1.377	26.6	68.0
chloropentafluorobenzene	0.885[f]	0.109	1.421	31.1	74.2
bromopentafluorobenzene	1.245[f]	0.155	1.449	33.4	77.4
iodopentafluorobenzene	1.23[f]	0.164	1.497	39.0	81.9
perfluorohexyliodide	1.41[f]	0.305	1.328	43.9	118.3
ethanol	0.55[g]	0.032	1.360	13.0	31.9
1-propanol	0.53[g]	0.040	1.384	17.5	42.2
N,*N*′-dimethylformamide	0.63[g]	0.049	1.431	20.0	46.8
diethyl ether	0.615[g]	0.064	1.353	22.7	51.5
1-butanol	0.465[g]	0.043	1.399	22.1	52.4
2-butanol	0.57[g]	0.052	1.397	22.1	52.4

[a] Calculated according to Bondi[27]. [b] Original data, ref 12. [c] Compilation of original and literature data, ref 16. [d] Mean value of data of ref 16 and ref 25. [e] Original data, ref 25. [f] Original data, ref 14. [g] Compilation of literature data, ref 25.

course, contribute less or nothing. It is possible to derive a size correction function $g(V_{vdW})$, if we consider the colliders simply as spheres of uniform polarizability. The overall surface of the collider is proportional to $V_{vdW}^{2/3}$. The transient shift of electron density into the $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 can only take place in the small contact region of O_2 and collider, where the MOs mutually overlap. As long as the area of the contact region is constant in the series of colliders, its relative magnitude varies with the collider size proportional to $V_{vdW}^{-2/3}$. Therefore, $g(V_{vdW}) = V_{vdW}^{-2/3}$ is proportional to that part of the collider polariz-

TABLE 2: Effect of the Collider on the b → a Radiative Transition of O_2, Data of Fink et al.[4]

collider	k^c_{b-a}, M^{-1} s^{-1}	R, mL mol^{-1}	V_{vdW},[a] mL mol^{-1}
Ne	0.6	1.0	9.2
Ar	10.2	4.1	16.8
Kr	21.6	6.2	20.8
Xe	46.8	10.1	25.4
N_2	7.8	4.3	15.8
O_2	9.0	4.0	13.0
SF_6	26.4	11.3	46.8
SO_2	31.8	9.7	27.2
PCl_3	252	26.1	47.2

[a] Calculated according to Bondi.[27]

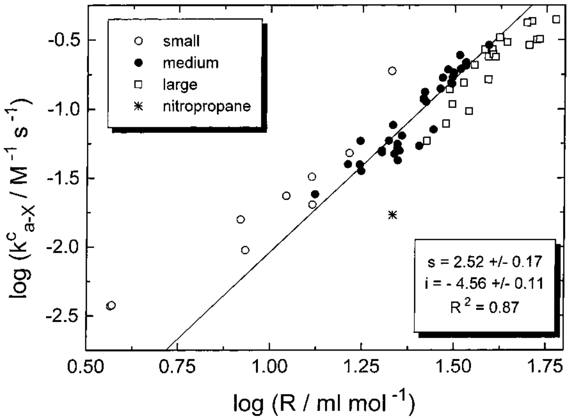

Figure 1. Double-logarithmic plot of k^c_{a-X} vs the molar refraction R of collider; data of Table 1; straight line represents linear least-squares fit for medium size colliders; for details see text.

ability which becomes effective in the collision-induced a → X radiative transition.

Two further quantities influence the magnitude of k^c_{a-X}.

(1) k^c_{a-X} is proportional to the normalized collision frequency Z, which can be calculated for spherical colliders by eq 2.

$$Z = d_{OC}^2 \, N_A \sqrt{8\pi kT/\mu} \qquad (2)$$

$d_{OC} = (d_{O2} + d_C)/2$ and μ are the collision distance and the reduced mass of the colliding pair, which can be calculated from $d_{O2} = 3.45$ Å, $d_C = (6V_{vdW}/\pi N_A)^{1/3}$ and the respective molecular weights. N_A is Avogadro's number, k the Boltzmann constant, and T the Kelvin temperature. The collision frequency in the liquid phase is by the value of the pair distribution function at contact distance larger than the gas phase value Z.[30] Assuming the model of hard sphere liquids, such values could be estimated, if the compressibilities of the liquids were known.[31,32] However, since for most of the investigated solvents compressibility data are lacking, we only calculate the normalized gas phase collision frequency, which varies moderately from 1.5×10^{11} (D_2O) to 2.5×10^{11} ($C_6F_{13}I$) M^{-1} s^{-1}.

(2) We have to keep in mind that the investigations have been done in liquids of strongly varying refractive index: $1.290 \le n \le 1.743$. The radiative rate constant of a dissolved species is expected to be proportional to the square of the refractive index of the surrounding medium.[33] In fact, this relation has been confirmed experimentally.[34]

Thus, for constant refractive index and collider size the probability of the induced a → X radiative transition per collision should be proportional to the function $f_{a-X}(R) = k^c_{a-X}/(Zn^2g(V_{vdW}))$, which still should depend on R. Figure 2 plots $\log(f_{a-X}(R))$ vs $\log(R)$.

A very strong and rather smooth linear correlation is observed. The slope of the linear least-squares fit of Figure 2 amounts to 2.05 ± 0.06. Thus, the analysis leads to the same result as our most recent investigation (slope 2.06 ± 0.08)[12] resting on data for 13 solvents. The residual scatter of the data around the fitted straight line results in part from the uncertainty of the experimental data but certainly also from the crudeness of the above made assumptions. Particularly, the consideration of the colliders as spheres of uniform polarizability is far apart from reality. The mobility of electron density varies not only with the collider but also with the atomic position on the collider molecule.

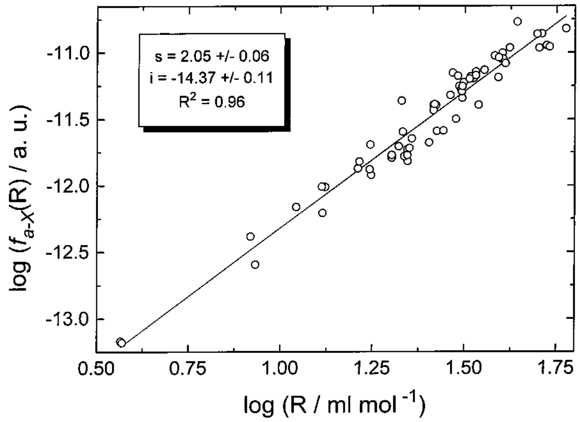

Figure 2. Double-logarithmic plot of $f_{d-X}(R)$ vs the molar refraction R of collider; straight line represents linear least-squares fit; for details see text.

For example, such collisions of $O_2(^1\Delta_g)$ with perfluorohexyliodide, for which O_2 is in contact with the carbon-bound fluorine atoms, are expected to enhance the a → X radiative transition much less than collisions of O_2 with the carbon-bound iodide atom, which has a much larger atomic polarizability (R((C)−I): 13.9, R((C)−F): 0.81 mL mol^{-1}).[35] Since the probability of the radiative transition increases with the square of the polarizability, vide infra, it is therefore not surprising that the value of $\log(f_{a-X}(R))$ for perfluorohexyliodide at $\log(R) = 1.642$ lies distinctly above the fitted line. For CS_2 an even larger deviation of $\log(f_{a-X}(R))$ from the fit to positive values is observed at $\log(R) = 1.329$. This maximum positive deviation is the consequence of the linear structure of CS_2. Since the surface of a cylindrical body is larger than the surface of a spherical body of the same volume, the molecular polarizability of the real CS_2 molecule enhances the radiative transition in collisions with O_2 much more strongly than a hypothetical spherical collider of the same value of R.

The fact that the probability of the collision-induced a → X radiative transition depends on the collision geometry has important implications for the analysis of the solvent dependent red-shift $\Delta\nu_{a-X}$ of the phosphorescence of $O_2(^1\Delta_g)$.[36−40] The average phosphorescence energy should approximately be given by the energy difference of solvated 1:1 collision complexes $O_2(^1\Delta_g)M$ and $O_2(^3\Sigma_g^-)M$. Hereby, the geometry of the $O_2(^1\Delta_g)M$ complex emitting with maximum probability is determined by the maximum possible shift of electron density into the $\pi_{g,z}$ and $\pi_{g,y}$ MOs of O_2 but not by the minimum of complex energy.[40] Therefore, only the energy differences of the collision complexes $O_2(^1\Delta_g)M$ and $O_2(^3\Sigma_g^-)M$ with maximum charge shift are of interest in the analysis of $\Delta\nu_{a-X}$.

The general correlation of Figure 2 with slope 2 demonstrates that the probability of the collision-induced a → X radiative transition is proportional to the square of the molecular polarizability of the collider, if the effects of collision frequency, refractive index, and collider size are removed. The correlation

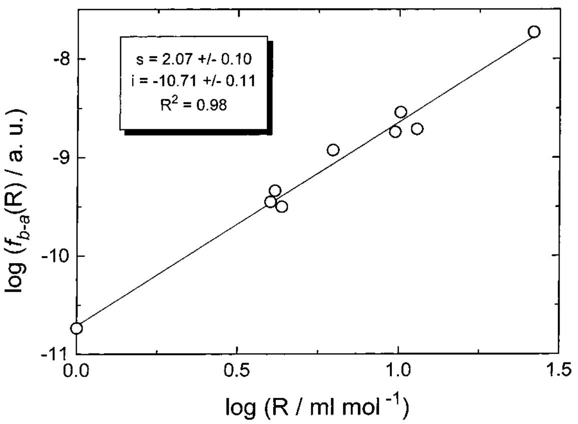

Figure 3. Double-logarithmic plot of $f_{b-a}(R)$ vs the molar refraction R of collider; straight line represents linear least-squares fit; for details see text.

includes colliders of very different ionization potential. Since no systematic deviation from linearity is seen, which depends on IP, we conclude that CT interactions play only a minor role for the enhancement of the a → X emission.

As was already mentioned by Darmanyan,[25] it is interesting to note that heavy-atom effects on k_{a-X} are not observed. The investigation of the general correlation of Figure 2 demonstrates that the experimental data of $\log(f_{a-X}(R))$ of most iodide- or bromine-substituted colliders deviate slightly from the fitted straight line to to larger values, which already can be explained by the neglect of the real molecular structure of the colliders in the present analysis, vide infra. Thus, also the analysis of the k^{c}_{a-X} data reveals no external heavy-atom effect on the collision induced a → X transition. According to Darmanyan,[25] the missing heavy-atom effect seems to contradict the SOC-mediated perturbation model of Minaev. However, Minaev did not postulate such an effect.[28,29] It seems that the missing external heavy-atom effect on the collision-induced a → X transition is probably the consequence of the fact that the internal perturbation of O_2 by SOC is much stronger than the external perturbation induced by SOC of a heavy-atom-substituted collider.

Finally, bimolecular rate constants of the collision-induced b → a transition are analyzed. The data, which have been determined by Fink et al.,[4] are listed in Table 2. The function $f_{b-a}(R) = k^{c}_{b-a}/(Zn^2 g(V_{vdW}))$, is proportional to the probability of the induced b → a radiative transition per collision for constant refractive index and collider size. Since the data of k^{c}_{b-a} have been measured in the diluted gas phase, the refractive index of the surrounding medium was always $n = 1$. However, $f_{b-a}(R)$ should still depend on the molecular polarizability of the collider. Figure 3 plots $\log(f_{b-a}(R))$ vs $\log(R)$.

Again we observe a strong linear correlation. The slope 2.07 ± 0.10 of the linear least-squares fit is in the limits of mutual uncertainty the same as determined in the corresponding correlation of Figure 2 for the data of the a → X transition. Thus, we obtain parallels with slope 2. Since rate constants of radiative transitions are proportional to the square of the transition moments, we realize that the transition moments of both collision-induced radiative transitions of O_2 are directly proportional to the molecular polarizability of the collider for constant collider size and collision frequency.

This result is surprisingly simple but reasonable. Minaev derived $\mathbf{M}_{b-a} = 0.5(M_x - M_y)$ and $\mathbf{M}_{a-X} = -C\mathbf{M}_{b-a}$, whereby M_x and M_y are the dipole moments induced into the $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 during the collision.[29] Hence, the transition moments of the b → a and a → X transitions should both depend linearly on the difference $M_x - M_y$. We find for both transition moments the same dependence on R: $\mathbf{M}_{a-X} \sim R$ and $\mathbf{M}_{b-a} \sim R$. Our results demonstrate that the difference of the induced dipole moments is directly proportional to the *molecular polarizability of the collider*. Therefore, the transient shift of electron density from collider MOs into the only partially filled $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 postulated by Minaev is verified by our findings.

Dipole moments cannot only be induced by this pure dispersion interaction but, of course, also by induction interaction of permanent collider dipole moments with the nonpolar O_2 molecule. This induction interaction, which depends on the *molecular polarizability of* O_2, also leads to a different polarization of the $\pi_{g,x}$ and $\pi_{g,y}$ MOs and should therefore also contribute to the enhancement of the radiative transitions. However, since any polarity effect disappears behind the strong dependence of k^{c}_{a-X} on the molecular polarizability of the collider, the pure dispersion interaction must be much stronger than the induction interaction. This conclusion is confirmed by calculations performed for simple molecules, which show that dispersion interactions are much stronger than induction interactions.[41]

It should be noted that most colliders of Table 2 are small. $V_{vdW} \leq 27.2$ mL mol^{-1} for Ne, Ar, Kr, Xe, N_2, O_2, and SO_2. The fact that we still find the slope 2 for the plots of $\log(f_{b-a}(R))$ and $\log(f_{a-X}(R))$ vs $\log(R)$ shows that the size correction function $g(V_{vdW})$ works well also for colliders of similar (O_2, N_2, Ar, Kr, CH_3OH, HCOOH, Xe) or even smaller (Ne, H_2O, D_2O) size than O_2. Since also for these small colliders $g(V_{vdW}) = V_{vdW}{}^{-2/3}$ holds true, the region of mutual overlap of the collider MOs and the $\pi_{g,x}$ and $\pi_{g,y}$ MOs of O_2 must actually be rather small. Obviously, the transient shift of electron density inducing the radiative transition occurs in a very restricted region, which covers only few collider MOs.

The linear fits of Figures 2 and 3 with intercepts i allow the calculation of an average general value of the ratio $f_{a-X}(R)/f_{b-a}(R)$, which should be equal to the ratio $C^2E_{\Delta}{}^3/(E_{\Sigma} - E_{\Delta})^3$. For $\log(R) = 1$, where we have an overlap of the data of $\log(f_{a-X}(R))$ and $\log(f_{b-a}(R))$, we obtain $f_{a-X}(R)/f_{b-a}(R) = 2.1 \times 10^{-4}$. This result is distinctly smaller than the theoretically derived ratio 6.1×10^{-4} and the average experimental ratio of 6×10^{-4} obtained by us in liquid phase measurements of k^{c}_{a-X} and k^{c}_{b-a} for CCl_4, C_2Cl_4, and C_4Cl_6.[12,29] The deviation is probably caused by the different techniques of determination of k^{c}_{a-X} and k^{c}_{b-a}. For example, in our previous study k^{c}_{a-X} and k^{c}_{b-a} have been determined in emission experiments in reference to the quantum yield of the a → X phosphorescence of $O_2(^1\Delta_g)$ in benzene, which amounts to $Q_{a-X}(\mathrm{BNZ}) = (4.7 \pm 1.7) \times 10^{-5}$.[8,12] The rather high uncertainty of ±33% of the standard cancels, if liquid phase data of k^{c}_{a-X} are compared with liquid phase data of k^{c}_{b-a}, but rests and adds to the systematic experimental errors of the k^{c}_{b-a} determination, if values of k^{c}_{a-X} from liquid phase emission measurements are compared with k^{c}_{b-a} data obtained by different techniques. Actually, all k^{c}_{b-a} data of Fink et al.[4] carry the uncertainty of the rate constant of the unperturbed b → a emission, which could be considerable.[2-4] Therefore, the three times smaller ratio $f_{a-X}(R)/f_{b-a}(R) = 2.1 \times 10^{-4}$, resulting from the analysis which includes the k^{c}_{a-X} data of Fink et al., could well be the consequence of the addition of systematical experimental errors. In fact, the first a → b absorption measurements of $O_2(^1\Delta_g)$ in solution performed by Weldon and Ogilby[10] led to ratios $k_{b-a}/k_{a-X} = C^2E_{\Delta}{}^3/(E_{\Sigma} - E_{\Delta})^3$, which are by about 50% larger than the theoretical value of 6.1×10^{-4}. However, also in this case the systematical errors add up, because of the different techniques used (emission for k_{a-X}, absorption for k_{b-a}). This important aspect has been overlooked in ref 10.

Conclusions

The analysis of a large set of experimental data on a molecular level revealed the principal mechanism of the collision-induced enhancement of the a → X and b → a radiative transitions. After having removed the effects of refractive index, collision frequency, and collider size from the bimolecular rate constants, we discover that the transition moments of both collision-induced radiative transitions of O_2 are directly proportional to the molecular polarizability of the collider. According to Minaev two effects cooperate.[28,29] (1) The asymmetric shift of electron density from the collider into the $\pi_{g,x}$ and $\pi_{g,y}$ molecular orbitals of O_2 induces transient dipole moments M_x and M_y of different magnitude, which, as we found, are directly proportional to the molecular polarizability of the collider. Hereby, electric dipole character is induced into the b → a transition. (2) Because of the strong SOC of O_2, the a → X transition profits proportionally from the enhancement of the b → a transition by intensity borrowing.

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